Modeling and analysis of non-isothermal chemical reaction networks

Wang, Li

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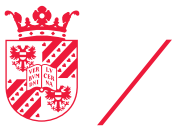
A port-Hamiltonian and contact geometry approach

LI WANG



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Modeling and Analysis of Non-isothermal Chemical Reaction Networks

A port-Hamiltonian and contact geometry approach

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To Wuming, Zhanming and Jinsheng

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Li WANG
Beijing
March 8, 2018

Contents

List of symbols

$\mathbb{R}$	real numbers
$\mathbb{R}^m$	the space of m-dimensional real vectors
$\mathbb{R}^m_+$	the space of m-dimensional real vectors with strictly positive entries
$\mathbb{N}$	natural numbers
$\mathcal{M}$	manifold $\mathcal{M}$
$\operatorname{im} C$	image of matrix C
$\ln x$	logarithm of x
$\exp x$	exponential of x
$\det C$	the determinant of matrix C
C^{tr}	transpose of matrix C
$\sum_{i=1}^{n} x_i$	the sum of x_i, $i = 1, \ldots, n$
$\prod_{i=1}^{n} x_i$	the product of x_1, $i = 1, \ldots, n$
∞	infinity
$\mathcal{C}^\infty$	the space of infinitely differentiable functions
$\operatorname{diag}(x_i)$	the diagonal matrix composed of x_i
$\bigcup$	arbitrary union of sets
e	Euler's number
$\square$	end of proof
$\varnothing$	the empty set
$\wedge$	wedge product
$f \circ g$	the composition of the functions f and g
$\frac{\partial f}{\partial x}$	the partial derivative of function f with respect to variable x
$\dot{x}$	the time-derivative of a vector x
$\mathbf{0}_{i \times i}$	the $i \times i$ zero matrix

I_i	the $i \times i$ identity matrix
$\mathbf{0}_i$	$i \times 1$ zero vector

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Chapter 1

Introduction

1.1 Motivation and previous work

The modeling and analysis of chemical reaction networks has been the subject of intensive research since its foundation in the 1970s, see (Horn and Jackson 1972), (Horn 1972) and (Feinberg 1972), due to the widespread application of large-scale chemical reaction networks in various application areas. For example, in (Nemes et al. 1977), a possible construction of a complex chemical reaction network is introduced base on the fact that we can define the kinetic communication as a transfer of atoms between the species and determine all the kinetic communications occurring in the possible mechanism of a complex chemical process; in (Feinberg 1987), the dynamics of complex isothermal reactors are studied in general terms with special focus on connections between reaction network structure and the capacity of the corresponding differential equations to admit unstable behavior; in (Polettini et al. 2015), the effect of intrinsic noise on the thermodynamic balance of complex chemical reaction networks has been studied; in (Rao and Esposito 2016), the non-equilibrium thermodynamic description has been built for open chemical reaction networks which is driven by time-dependent chemostats. However, even though many advances have been made for the modeling and analysis of the isothermal chemical reaction networks, the study of non-isothermal chemical reaction networks still poses fundamental challenges.

In order to model the chemical reaction networks, in this dissertation, we will make use of one of the most basic laws prescribing the dynamics of the the concentrations of the various species, called the *law of mass action*. This provides the foundation of a structural theory of isothermal chemical reaction networks governed by *mass action kinetics*. Since this mathematical structure is a good way to get insight into the dynamical properties of isothermal chemical reaction networks, a series of papers about the modeling and analysis of mass action kinetics chemical reaction networks arose, see for example (Rao et al. 2014), (Jayawardhana et al. 2012), (Balabanian and Bickart 1981), (Varma and Palsson 1994).

In this dissertation, we will use different approaches to the modeling and analysis of the non-isothermal mass action kinetics chemical reaction networks. Generally speaking, these approaches can be divided into two classes: one based on the port-Hamiltonian system theory in Chapters 2, 3, and 4, and the other based on the theory of contact systems in Chapter 5. In the modeling of non-isothermal chemical reaction networks, we need to take more variables into the consideration, which are related to the thermodynamic process occurring in the reactor, such as the temperature, the entropy, the internal energy and the chemical potentials, etc..

Port-Hamiltonian system theory, as a powerful tool for the control of multi-physics systems, has been intensively employed in the modeling and control since its foundation in 1990s, see (Maschke and van der Schaft 1991), (van der Schaft and Maschke 1995) and (van der Schaft 2006). More recently, a quasi port-Hamiltonian modeling, namely *Irreversible port-Hamiltonian System* (IPHS), was introduced in (Ramirez, Maschke and Sbarbaro 2013b). Thanks to its formulation which is directly related with the energy and entropy functions, this quasi port-Hamiltonian formulation provides a nature way to model thermodynamic processes. Therefore we are interested in applying it to non-isothermal chemical reaction networks. Moreover, we will see that the quasi port-Hamiltonian formulation of non-isothermal chemical reaction networks is not only important for modeling, but for dynamical analysis as well. Furthermore, we will study the interconnection of the chemical reaction networks which is an interesting subject. So far, as we know, most of the previous work analyze the interconnection of the chemical reaction networks from the experimental perspective, see for example (Papachristodoulou and Recht 2007) and (Prior and Rosseinsky 2003). In this dissertation, we get the inspiration from (van der Schaft et al. 2013a) and use the port-Hamiltonian theory for the modeling of interconnected chemical reaction networks.

Another approach that will be studied in this dissertation, is the theory of contact systems, continuing on previous work. The contact structure is defined as a canonical differential-geometric structure underlying Gibbs' relation and the input-output contact systems are defined as one of the geometric representations of those thermodynamic systems in (Arnold 1989), (Eberard et al. 2007), (Libermann and Marle 1987). Necessary conditions for the stability of the linearisation of contact vector fields were given in (Favache et al. 2009). More recently, a new framework of conservative contact systems, together with a class of structure-preserving feedbacks, has been proposed in (Ramirez, Maschke and Sbarbaro 2013a). With respect to a specific modified contact form, it is possible to render the controlled contact system again a contact system. Moreover, due to its contact geometry directly related to Gibbs' relation, it has been proved that the theory of contact systems is also a good approach for the modeling and analysis of thermodynamic process, such as the *con-*

tinuous stirred tank reactor (CSTR). Hence, in this part, we have two challenges. One is to study the conditions under which the structure-preserving feedback can be formalized as expected, and another is to apply the theory of contact systems with structure-preserving feedback to non-isothermal chemical reaction networks.

1.2 Contribution of the thesis

The main contributions of each chapter can be summarized as follows.

- ***Chapter 2:*** The stability of the irreversible port-Hamiltonian, introduced in (Ramirez, Maschke and Sbarbaro 2013b), is studied in this chapter. Especially for modeling of non-isothermal chemical reaction networks, this irreversible port-Hamiltonian system, expressing the laws of thermodynamics, offer us an approach to study the thermodynamic properties of non-isothermal chemical reactions. This chapter is based on (Wang et al. 2016).

- ***Chapter 3:*** First, based on mass balance and energy balance equations, a port-Hamiltonian formulation for non-isothermal mass action kinetics chemical reaction networks which are detailed balanced is developed. This formulation directly extends the port-Hamiltonian formulation of isothermal chemical reaction networks of (van der Schaft et al. 2013a) and (van der Schaft et al. 2013b), in contrast with the irreversible port-Hamiltonian formulation in Chapter 2. It exhibits the energy balance and the thermodynamic principles in an explicit way. Based on the obtained port-Hamiltonian formulation, we provide a thermodynamic analysis of the existence and characterization of thermodynamic equilibria and their asymptotic stability. Being directly related with the energy and entropy functions, this port-Hamiltonian formulation is easily applicable to chemical and biological systems. The second contribution of this chapter is the extension of the port-Hamiltonian formulation and the thermodynamic analysis to non-isothermal chemical reaction networks with external ports. This chapter is based on (Wang et al. 2018).

- ***Chapter 4:*** Based on the quasi port-Hamiltonian formulation developed in Chapter 3 and making use of different approaches to interconnection, it is proved that we can develop two different classes of port-Hamiltonian systems to model interconnected chemical reaction networks. Moreover, it is proved as well that through the elimination of mass action kinetics and power port constraints, the two modeling approaches are equivalent. This provides flexibility for the modeling of chemical reaction networks, depending on the spe-

cific physical structure of systems. This chapter is based on (Wang et al. n.d.) (to be submitted).

- ***Chapter 5:*** The main contribution of this chapter is the stabilization of the controlled contact system by means of structure-preserving feedback. It is shown in this chapter how to formalize the structure-preserving feedback, the modified contact Hamiltonian and the invariant stable Legendre submanifold. This chapter is based on (Wang et al. 2015).

1.3 Outline of the thesis

The thesis is divided into four chapters.

In Chapter 2 we start by introducing port-Hamiltonian systems and a class of quasi port-Hamiltonian system generated by the total internal energy, so called irreversible port-Hamiltonian system. We apply the concept of irreversible port-Hamiltonian systems to the modeling of non-isothermal chemical reaction networks, which are governed by mass action kinetics. We perform its stability analysis, including the conditions for existence of a thermodynamic equilibrium and their asymptotic stability.

In Chapter 3 we aim to develop a new class of port-Hamiltonian system which can be used for the modeling of non-isothermal mass action kinetics chemical reaction networks. This quasi port-Hamiltonian system is generated by the total entropy. As did in the previous chapter, a thermodynamic analysis is carried out, including the characterization of equilibria and the asymptotic stability. This chapter ends with the extension of this quasi port-Hamiltonian formulation to non-isothermal chemical reaction networks with external ports.

In Chapter 4 we extend the study of the quasi port-Hamiltonian system in Chapter 3 to the modeling of the interconnection of two chemical reaction networks governed by mass action kinetics. Here we offer two different modeling approaches for the interconnection of chemical reaction networks in quasi port-Hamiltonian form of interconnected chemical reaction networks. The difference between this two modeling approaches is due to the different assumption of the way of interconnection.

In Chapter 5 we analyze the controlled contact system with the structure-preserving feedback. A series of control synthesis will be studied in order to add some constraints while choosing the structure-preserving state feedback. First, some studies of local stability is carried out to determine the structure-preserving state feedback, through the equilibrium conditions for the closed-loop contact system and the Jacobian matrix of the closed-loop contact vector field. Second, conditions for lo-

cal and partial stability on closed-loop invariant Legendre submanifold are given, in order to determine the controlled contact Hamiltonian and to verify the correctness of the structure-preserving feedback.

In Chapter 6 a general conclusion and recommendations for future research are given.

1.4 Notation

The following notations are used throughout the text.

- The element-wise product of two vectors $xz \in \mathbb{R}^m$ is defined as $(xz)_i := x_i z_i$, $i = 1, \ldots, m$.
- The element-wise quotient of two vectors $\frac{x}{z} \in \mathbb{R}^m$ is defined as $(\frac{x}{z})_i = \frac{x_i}{z_i}$, $i = 1, \ldots, m$.
- The element-wise natural logarithm $\mathrm{Ln} : \mathbb{R}^m_+ \to \mathbb{R}^m$, $x \mapsto \mathrm{Ln}(x)$, is defined as the mapping whose ith component is given as $(\mathrm{Ln}(x))_i := \ln(x_i)$. $\mathrm{Ln}(xz) = \mathrm{Ln}(x) + \mathrm{Ln}(z)$, and $\mathrm{Ln}(\frac{x}{z}) = \mathrm{Ln}(x) - \mathrm{Ln}(z)$.
- The element-wise natural exponential $\mathrm{Exp} : \mathbb{R}^m_+ \to \mathbb{R}^m$, $x \mapsto \mathrm{Exp}(x)$, is the mapping whose ith component is given as $(\mathrm{Exp}(x))_i := \exp(x_i)$. $\mathrm{Exp}(x + z) = \mathrm{Exp}(x)\mathrm{Exp}(z)$.
- The mapping $\mathrm{Diag} : \mathbb{R}^m \to \mathbb{R}^{m \times m}$, $v \mapsto \mathrm{Diag}(v)$, where $\mathrm{Diag}(v)$ is the diagonal matrix with $(\mathrm{Diag}(v))_{ii} = v_i$.

Chapter 2

Irreversible port-Hamiltonian formulation generated by the internal energy

2.1 Introduction

With its great potential in various application domains, the analysis of the dynamics of chemical reaction networks has been a popular subject in recent years, see (Craciun and Pantea 2008) and (Conradi et al. 2005). For example, much progress has been made on the mathematical structure of isothermal chemical reaction networks governed by mass action kinetics, see (van der Schaft et al. 2013a), (van der Schaft et al. 2015) and (Rao et al. 2013); the feasibility conditions to identify admissible equilibria for weakly reversible mass action law systems has been studied in (Alonso and Szederkényi 2016) and Wegsheider conditions that restrict the possible set of equilibrium under a detailed balance condition has been discussed in (Alonso and Otero-Muras 2017). Nevertheless, for the non-isothermal case there remain major challenges. As we know, in the non-isothermal case, the thermodynamic principles of chemical reaction networks should be taken into consideration when we investigate its modeling and stability analysis.

Port-Hamiltonian systems (PHS), which is a very powerful tool for the control of multi-physics systems, has been intensively employed in modeling and for passivity-based control (PBC) of electrical, mechanical and electromechanical domains (Maschke and van der Schaft 1991), (van der Schaft and Maschke 1995) and (van der Schaft 2006). More recently, a quasi PHS model, namely Irreversible port-Hamiltonian System, was proposed (Ramirez, Maschke and Sbarbaro 2013b). Thanks to its formulation which is directly related with the energy and entropy functions, IPHS could be easily utilized for thermodynamic, chemical and biological systems. Therefore we are naturally inspired to apply it to non-isothermal chemical reaction networks.

In this chapter, we implement some results of the theory of IPHS and its stability analysis to a non-isothermal chemical reaction network. Beginning with the mathematical structure of chemical reaction networks in the non-isothermal case, we establish its IPHS formulation and then investigate the set of equilibria and their asymptotic stability.

The chapter is organized as follows. Sect. 2.2 presents the mathematical structure of non-isothermal chemical reaction networks. Sect. 2.3 deals with the framework of IPHS and its specialization to non-isothermal chemical reaction networks, and Sect. 2.4 with the analysis of the property of *detailed balance*, including the set of equilibria and the energy based *availability function* generated by the internal energy. In Sect. 2.5, we demonstrate the effectiveness of our proposed approach by applying it on a simple non-isothermal chemical reaction network.

2.2 Chemical reaction network structure

In this section, we first survey some definitions about chemical reaction networks discussed in (Ramirez, Maschke and Sbarbaro 2013b), (Couenne et al. 2006) and (van der Schaft et al. 2013a) which will be used in the following paragraphs.

The basis of *chemical reaction network theory*, originated in the 1970s, can be described as follows. Consider a chemical reaction network composed by r *chemical reactions*, m *chemical species* and c *complexes* with $r, m, c \in \mathbb{N}$. Such chemical reaction network can be represented by the following reversible reaction scheme:

$$\sum_{i=1}^{m} \alpha_{ij} X_i \overset{j}{\rightleftharpoons} \sum_{i=1}^{m} \beta_{ij} X_i, j = 1...r \tag{2.1}$$

with α_{ij}, β_{ij} being the constant stoichiometric coefficients for chemical species X_i of the jth chemical reaction. The graph-theoretic formulation, according to (Feinberg 1987), (Feinberg 1995), and (Horn and Jackson 1972), is to consider the chemical complexes defined by the left-hand and the right-hand sides of the chemical reactions, and to associate to each complex a vertex of a graph, while each reaction from left-hand to right-hand complex corresponds to a directed edge.

Remark 2.1. In (2.1), we use the symbol "$\rightleftharpoons$", which means that the chemical reaction networks considered in this dissertation are assumed to consist of reversible chemical reactions.

Then, we define a *state vector*, denoted as $x = [x_1, x_2..., x_m]^{tr} \in \mathbb{R}^m_+$ where x_i denotes the concentration of the ith species (denoted as X_i in (2.1)). By the *mass*

balance laws, the basic structure of the dynamics of x can be written as

$$\dot{x} = Cv \tag{2.2}$$

where C is an $m \times r$ matrix, called the *stoichiometric matrix*, whose (i, j)th element is the signed stoichiometric coefficient of the ith species in the jth reaction. Clearly, all elements of the stoichiometric matrix C are integers. If the ith species appears in the left-side of the jth reaction,the (i, j)th element of C is negative. On the contrary, if it is in the right-side of the jth reaction, the (i, j)th element of C is positive. Thus the stoichiometric matrix C expresses structure of the chemical reactions network. In fact, the stoichiometric matrix C can be decomposed as

$$C = ZB \tag{2.3}$$

where Z is an $m \times c$ matrix, called the *complex composition matrix* and B is the *incidence matrix* of the directed graph of complexes. Here we introduce the space of complexes as done in (Feinberg 1987), (Feinberg 1995), (Horn and Jackson 1972) and (Horn 1972). The space of complexes consists of the union of the left-hand or the right-hand sides of the chemical reactions in the network. The complex composition matrix, whose $i\rho$th element captures the expression of the ρth complex in the ith chemical species, is used to describe directly the relation between the space of complexes and the space of species. Clearly, all elements of the complex composition matrix Z are non-negative integers.

Remark 2.2. Complexes may show up in more than one reaction, and may appear as left-hand side in one chemical reaction and right-hand side in another chemical reaction.

The matrix B in (2.3) is an $c \times r$ matrix, called the incidence matrix of the graph of complexes. The incidence matrix B characterizes the directed graph of the chemical reaction network, and is defined as follows. The columns of B correspond to edges with a $+1$ at the position of the head vertex (the right side of the chemical reaction) and -1 at the position of the tail vertex (the left side of the chemical reaction), and 0 everywhere else.

For example, consider a chemical reaction network composed of three chemical reactions, involving the chemical species X_1,X_2, X_3 and X_4, given as

$$\begin{aligned} &X_1 + 2X_2 \rightleftharpoons X_3 \\ &X_3 \rightleftharpoons 2X_1 + X_2 \\ &X_3 + X_4 \rightleftharpoons X_2 \end{aligned} \tag{2.4}$$

The stoichiometric matrix C of this network is

$$C = \begin{bmatrix} -1 & 2 & 0 \\ -2 & 1 & 1 \\ 1 & -1 & -1 \\ 0 & 0 & -1 \end{bmatrix}$$

The complex composition matrix Z (with columns expressing the composition of each complex in the chemical species) is

$$Z = \begin{bmatrix} 1 & 0 & 2 & 0 & 0 \\ 2 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix}$$

The incidence matrix B is

$$B = \begin{bmatrix} -1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 1 \end{bmatrix}$$

Clearly, we have $C = ZB$.

Moreover, for the jth chemical reaction, let $Z_{\mathcal{S}_j}$ and $Z_{\mathcal{P}_j}$ denote the columns of the complex composition matrix Z corresponding to the substrate complex $\mathcal{S}_j$ and the product complex $\mathcal{P}_j$ (the left-hand and right-hand side of the jth reaction). Note that in this notation we have $\alpha_{ij} = Z_{i\mathcal{S}_j}$ and $\beta_{ij} = Z_{i\mathcal{P}_j}$. For the chemical reaction network (2.4), we have

$$\begin{aligned} Z_{\mathcal{S}_1} &= [\ 1 \quad 2 \quad 0 \quad 0\ ]^{tr} \\ Z_{\mathcal{P}_1} &= [\ 0 \quad 0 \quad 1 \quad 0\ ]^{tr} \\ Z_{\mathcal{S}_2} &= [\ 0 \quad 0 \quad 1 \quad 0\ ]^{tr} \\ Z_{\mathcal{P}_2} &= [\ 2 \quad 1 \quad 0 \quad 0\ ]^{tr} \\ Z_{\mathcal{S}_3} &= [\ 0 \quad 0 \quad 1 \quad 1\ ]^{tr} \\ Z_{\mathcal{P}_3} &= [\ 0 \quad 1 \quad 0 \quad 0\ ]^{tr} \end{aligned}$$

The vector $v \in \mathbb{R}^r$ in (2.2), called *the chemical reaction fluxes*, denotes the vector of chemical reaction rates. Let v_j be the jth element of v which denotes the chemical

reaction rate of the jth chemical reaction of the chemical reaction network. Then v_j is a combination of the forward chemical reaction and the backward chemical reaction, i.e., $v_j = v_j^f - v_j^b$. The forward and backward chemical reactions are assumed to satisfy the hypothesis of mass action kinetics. This means that the forward reaction rate is equal to

$$v_j^f = k_j^f(T) \prod_{i=1}^{m} {x_i}^{\alpha_{ij}}$$

and the backward reaction rate is given as

$$v_j^b = k_j^b(T) \prod_{i=1}^{m} {x_i}^{\beta_{ij}}$$

where the coefficients $k_j^f(T)$ and $k_j^b(T)$ follow *the Arrhenius equations*

$$k_j^f(T) = k_j^f \exp(-\frac{E_j^f}{RT}) \tag{2.5}$$

$$k_j^b(T) = k_j^b \exp(-\frac{E_j^b}{RT}), \tag{2.6}$$

where E_j^f, E_j^b are the *activity energies*, k_j^f and k_j^b the non-negative *forward and backward rate constants*, R the *ideal gas constant* (or the *Boltzmann constant*), and T is the temperature, see (Couenne et al. 2006).

As a consequence, the reaction rate of the jth chemical reaction of a chemical reaction network, can be written as

$$\begin{aligned} v_j(x,T) &= v_j^f(x,T) - v_j^b(x,T) \\ &= k_j^f(T) \prod_{i=1}^{m} x_i^{\alpha_{ij}} - k_j^b(T) \prod_{i=1}^{m} x_i^{\beta_{ij}} \\ &= k_j^f \exp(-\tfrac{E_j^f}{RT}) \prod_{i=1}^{m} x_i^{\alpha_{ij}} - k_j^b \exp(-\tfrac{E_j^b}{RT}) \prod_{i=1}^{m} x_i^{\beta_{ij}} \end{aligned} \tag{2.7}$$

where it is assumed that the forward and backward rate constants k_j^f and k_j^b, $j = 1, \cdots, r$, are both different from zero (all chemical reactions are assumed to be reversible).

Introducing $Z_{\mathcal{S}_j}$ and $Z_{\mathcal{P}_j}$, and using the mapping $\mathrm{Ln} : \mathbb{R}^m_+ \to \mathbb{R}^m$ as defined in Sect. 1.4, the reaction rate of the jth reaction of a chemical reaction network can be written as

$$\begin{aligned} v_j(x,T) &= k_j^f(T)\exp(Z_{\mathcal{S}_j}^{tr}\mathrm{Ln}(x)) - k_j^b(T)\exp(Z_{\mathcal{P}_j}^{tr}\mathrm{Ln}(x)) \\ &= k_j^f\exp(Z_{\mathcal{S}_j}^{tr}\mathrm{Ln}(x) - \tfrac{E_j^f}{RT}) - k_j^b\exp(Z_{\mathcal{P}_j}^{tr}\mathrm{Ln}(x) - \tfrac{E_j^b}{RT}) \end{aligned} \tag{2.8}$$

Remark 2.3. For an isothermal chemical reaction network, the rate coefficients k_j^f and k_j^b can be considered to be constant, and in the Arrhenius equations, $E_j^f = 0$ and $E_j^b = 0$, for $j = 1, \ldots, r$. Then the reaction rate of the jth chemical reaction simplifies to

$$\begin{aligned} v_j(x) &= v_j^f(x) - v_j^b(x) \\ &= k_j^f\prod_{i=1}^m x_i^{\alpha_{ij}} - k_j^b\prod_{i=1}^m x_i^{\beta_{ij}} \\ &= k_j^f\exp(Z_{\mathcal{S}_j}^{tr}\mathrm{Ln}(x)) - k_j^b\exp(Z_{\mathcal{P}_j}^{tr}\mathrm{Ln}(x)) \end{aligned} \tag{2.9}$$

2.3 Irreversible port-Hamiltonian formulation

In this section, we apply the irreversible port-Hamiltonian formulation of thermodynamical systems (Ramirez et al. 2014) and (Ramırez, Le Gorrec, Maschke and Couenne 2013), to the modeling of non-isothermal chemical reaction networks. This section has been published in (Wang et al. 2016).

We begin by recalling some notations and definitions from the theory of port-Hamiltonian as can be found in (van der Schaft et al. 2014), (Maschke and van der Schaft 1991) and (van der Schaft and Maschke 2011). The aim of the theory of port-Hamiltonian systems (PHS) is to provide a unified mathematical framework for the modeling of physical systems from different physical domains, such as mechanical systems, electrical systems, chemical systems, biological systems, etc..

In this dissertation, only finite-dimensional port-Hamiltonian systems are taken into consideration. On the state space $\mathbb{R}^m$, a port-Hamiltonian system can be written by the following state equation,

$$\dot{x} = \mathcal{J}(x)\frac{\partial \mathrm{H}}{\partial x}(x) + g(x)u \tag{2.10}$$

with $m \times m$ skew-symmetric interconnection matrix $\mathcal{J}(x) = -\mathcal{J}^{tr}(x)$, input matrix $g(x)$, input function $u \in \mathbb{R}^m$, and Hamiltonian function $\mathrm{H}(x) : \mathbb{R}^m \to \mathbb{R}$. For thermodynamic systems, the Hamiltonian function H represents usually the total energy U

of the system. The skew-symmetric matrix $\mathcal{J}$ defines a *pseudo-Poisson bracket*. From (van der Schaft and Maschke 1994) and (van der Schaft 2000), we know that if the skew-symmetric matrix $\mathcal{J}$ is constant in some local coordinates then it satisfies the *Jacobi identity*, and it defines a true Poisson bracket. The port-Hamiltonian dynamics (2.10) can be rewritten as

$$\begin{aligned} \dot{x} &= \{x, U\}_{\mathcal{J}} + g(x)u \\ &= \mathcal{J}(x)\tfrac{\partial U}{\partial x}(x) + g(x)u \end{aligned} \tag{2.11}$$

where $\{x, U\}_{\mathcal{J}}$ is the Poisson bracket. The Poisson bracket of two functions X and Y is expressed as

$$\{X, Y\}_{\mathcal{J}} = \frac{\partial X}{\partial x}^{tr}(x)\mathcal{J}(x)\frac{\partial Y}{\partial x}(x)$$

Clearly, the features of Poisson bracket, such as skew-symmetry and the Jacobi identities, relate to the conservation laws of the system. However, the irreversible transformations in thermodynamic systems, such as the entropy creation, can not be expressed in this structure. As a consequence, the port-Hamiltonian formulation is not sufficient to deal with the modeling of non-isothermal irreversible thermodynamic systems.

In recent works, a kind of quasi port-Hamiltonian systems, called irreversible port-Hamiltonian systems, have been proposed to model thermodynamic systems, thereby satisfying the first and second laws of thermodynamics. In general, the irreversible port-Hamiltonian formulation for non-isothermal irreversible thermodynamic systems, can be defined by the following equations (Ramirez 2012), (Ramirez, Maschke and Sbarbaro 2013b):

$$\dot{x} = \mathcal{R}(x, \frac{\partial U}{\partial x}(x), \frac{\partial S}{\partial x}(x))\mathcal{J}\frac{\partial U}{\partial x}(x) + W(x, \frac{\partial U}{\partial x}(x)) + g(x, \frac{\partial U}{\partial x}(x), u) \tag{2.12}$$

where $x \in \mathbb{R}^m$ is the state vector, $U : \mathbb{R}^m \to \mathbb{R}$ is the total internal energy of the system, and $S(x) : C^\infty(\mathbb{R}^m) \to \mathbb{R}$ is the entropy of system. Furthermore, $\mathcal{J} = -\mathcal{J}^{tr}$ is an $m \times m$ constant skew-symmetric matrix and $\mathcal{R} = \mathcal{R}(x, \frac{\partial U}{\partial x}, \frac{\partial S}{\partial x})$ is composed of a positive definite function and a Poisson bracket of S and U:

$$\mathcal{R}(x, \frac{\partial U}{\partial x}(x), \frac{\partial S}{\partial x}(x)) = \gamma(x, \frac{\partial U}{\partial x}(x))\{S, U\}_J \tag{2.13}$$

where finally $\gamma(x, \frac{\partial U}{\partial x}(x)) = \hat{\gamma}(x) : \mathbb{R}^m \to \mathbb{R}$, is a nonlinear positive function of the state and co-state of the system. Finally, the term $g(x, \frac{\partial U}{\partial x}(x), u)$ denotes the input matrix of the system.

Remark 2.4. The main feature of irreversible port-Hamiltonian dynamics expressed by (2.12) is that the function $\mathcal{R}(x, \frac{\partial U}{\partial x}(x), \frac{\partial S}{\partial x}(x))$ is dependent on the co-state variables $\frac{\partial U}{\partial x}(x)$. That means that in comparison with PHS, the linearity of the Poisson tensor (given by the symplectic structure) is destroyed.

In this dissertation, similar to (Ramirez, Maschke and Sbarbaro 2013b), we will rewrite the Irreversible port-Hamiltonian formulation in (2.12), in particular for chemical reaction networks as described in Sect. 2.2.

Theorem 2.5. *The dynamical equations of a chemical reaction network given by (2.1) can be expressed as an irreversible port-Hamiltonian system*

$$\begin{aligned} \dot{z} &= \left(\sum_{j=1}^{r} \mathcal{R}_j(z, \tfrac{\partial U}{\partial z}(z), \tfrac{\partial S}{\partial z}(z)) \mathcal{J}_j \right) \tfrac{\partial U}{\partial z}(z) + g(z, \tfrac{\partial U}{\partial z}(z), u) \\ &= \mathcal{J}_{\mathcal{R}}(z, \tfrac{\partial U}{\partial z}(z), \tfrac{\partial S}{\partial z}(z)) \tfrac{\partial U}{\partial z}(z) + g(z, \tfrac{\partial U}{\partial z}(z), u) \end{aligned} \tag{2.14}$$

with the state vector $z = [x, S]^{tr} = [x_1, \ldots, x_m, S]^{tr} \in \mathbb{R}^{m+1}$, the total internal energy $U(x)$ as Hamiltonian function, the co-state vector $\frac{\partial U}{\partial z} = [\mu_1, \ldots, \mu_m, T]^{tr} \in \mathbb{R}^{m+1}$, with μ_i the chemical potential of the ith chemical species, $i = 1, \ldots, m$, and the input port of the system given by $g(z, \frac{\partial U}{\partial z}, u) \in \mathbb{R}^{m+1}$.

The dynamics (2.14) can be considered as the sum of irreversible port-Hamiltonian dynamics of each chemical reaction in the chemical reaction network. According to the mass balance laws given by (2.2), for the jth chemical reaction in the chemical reaction network, the constant $(m+1) \times (m+1)$ skew-symmetric matrix $\mathcal{J}_j$ is expressed as

$$\mathcal{J}_j = \begin{bmatrix} 0 & \cdots & 0 & C_{1j} \\ \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & 0 & C_{mj} \\ -C_{1j} & \cdots & -C_{mj} & 0 \end{bmatrix}, \tag{2.15}$$

where C_{ij} is the (i,j)th element of the stoichiometric matrix C, $i = 1, \ldots, m$. The function $\mathcal{R}_j$ for the jth chemical reaction in the chemical reaction networks is expressed as

$$\mathcal{R}_j = \gamma_j(z, \frac{\partial U}{\partial z})\{S, U\}_{\mathcal{J}_j} = (\frac{v_j}{T\mathcal{A}_j})\mathcal{A}_j \tag{2.16}$$

with

$$\begin{aligned}
\gamma_j(z, \tfrac{\partial U}{\partial x}) &= \tfrac{v_j}{T\mathcal{A}_j} \\
\mathcal{A}_j &= \{S, U\}_{J_j} \\
&= \tfrac{\partial S}{\partial z}^{tr}(x)\mathcal{J}_j \tfrac{\partial U}{\partial z}(z) \\
&= \begin{bmatrix} 0 & \dots & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & \cdots & 0 & C_{1j} \\ \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & 0 & C_{mj} \\ -C_{1j} & \cdots & -C_{mj} & 0 \end{bmatrix} \begin{bmatrix} \mu_1 \\ \vdots \\ \mu_m \\ T \end{bmatrix} \\
&= -\sum_{i=1}^{m} C_{ij}\mu_i \\
v_j &= k_j^f \exp(Z_{\mathcal{S}_j}^{tr}\mathrm{Ln}(x) - \tfrac{E_j^f}{RT}) - k_j^b \exp(Z_{\mathcal{P}_j}^{tr}\mathrm{Ln}(x) - \tfrac{E_j^b}{RT})
\end{aligned} \tag{2.17}$$

where $\mathcal{A}_j$ is the chemical affinity of the jth chemical reaction, which corresponds to the thermodynamic driving force of the chemical reaction. Furthermore, v_j is the reaction rate of the jth chemical reaction based on the equation (2.8). Based on the definition of the chemical reaction rate vector mentioned in Sect. 2.2, $v = [v_1, \dots, v_r]^{tr} \in \mathbb{R}^r$. Let $\mathcal{R} = [\mathcal{R}_1, \dots, \mathcal{R}_r]^{tr} \in \mathbb{R}^r$, then $\mathcal{R} = \frac{v}{T}$ and the term $\mathcal{J}_\mathcal{R}$ can be expressed as

$$\begin{aligned}
\mathcal{J}_\mathcal{R} &= \sum_{j=1}^{r} \mathcal{R}_j(z, \tfrac{\partial U}{\partial z}, \tfrac{\partial S}{\partial z})\mathcal{J}_j \\
&= \begin{bmatrix} 0 & \cdots & 0 & \\ \vdots & \ddots & \vdots & C\mathcal{R} \\ 0 & \cdots & 0 & \\ -\mathcal{R}^{tr}C^{tr} & & 0 & \end{bmatrix}
\end{aligned} \tag{2.18}$$

Furthermore, the energy and entropy balance laws can be written as

$$\dot{U} = U_{in} - U_{out} \tag{2.19}$$

$$\dot{S} = S_{in} - S_{out} + \sigma \tag{2.20}$$

where U_{in} and U_{out} are respectively the energy taken into the reactor and taken out to external environments; σ the entropy creation which is irreversible due to mass transfer, heat transfer and the chemical processes occurring in the chemical reaction

network, and S_{in} and S_{out} are respectively the entropy flowing into the reactor by external sources, and flowing out of the reactor to the external environment. Then the input of IPHS for chemical reaction network is given as

$$g(z, \frac{\partial U}{\partial z}, u) = \begin{bmatrix} F_{in} - F_{out} \\ S_{in} - S_{out} \end{bmatrix}$$

where $F_{in} = [F_{in}^1 \dots, F_{in}^m]^{tr} \in \mathbb{R}^m$ and $F_{out} = [F_{out}^1, \dots, F_{out}^m]^{tr} \in \mathbb{R}^m$ denote the vector of inlet/outlet concentrations.

Consequently, the irreversible port-Hamiltonian formulation for a chemical reaction network in (2.14) can be formulated as

$$\begin{bmatrix} \dot{x}_1 \\ \vdots \\ \dot{x}_m \\ \dot{S} \end{bmatrix} = \begin{bmatrix} 0 & \cdots & 0 & \\ \vdots & \ddots & \vdots & C\mathcal{R} \\ 0 & \cdots & 0 & \\ -\mathcal{R}^{tr}C^{tr} & & 0 & \end{bmatrix} \begin{bmatrix} \mu_1 \\ \vdots \\ \mu_m \\ T \end{bmatrix} + \begin{bmatrix} F_{in}^1 - F_{out}^1 \\ \vdots \\ F_{in}^m - F_{out}^m \\ S_{in} - S_{out} \end{bmatrix} \tag{2.21}$$

Remark 2.6. If $g(z, \frac{\partial U}{\partial z}, u) = 0$, then the skew-symmetry of the matrix $\mathcal{J}_j, j = 1, \dots, r$, ensures that the total internal energy of the system is conserved. In order to compute the entropy balance, we write

$$\begin{aligned} \frac{dS}{dt} &= \frac{\partial^{tr} S}{\partial z} \dot{z} \\ &= \frac{\partial^{tr} S}{dz} \mathcal{J}_{\mathcal{R}}(z, \frac{\partial U}{\partial z}, \frac{\partial S}{\partial z}) \frac{\partial U}{\partial z}(z) \\ &= \begin{bmatrix} 0 & \dots & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & \cdots & 0 & \\ \vdots & \ddots & \vdots & C\mathcal{R} \\ 0 & \cdots & 0 & \\ -\mathcal{R}^{tr}C^{tr} & & 0 & \end{bmatrix} \begin{bmatrix} \mu_1 \\ \vdots \\ \mu_m \\ T \end{bmatrix} \\ &= -\mathcal{R}^{tr}C^{tr}\mu \\ &= \sum_{j=1}^{r} \sigma_j \\ &= \sigma \end{aligned}$$

with $\mu = [\mu_1, \dots, \mu_m]^{tr} \in \mathbb{R}^m$ the vector of chemical potentials, σ_j the irreversible entropy creation due to the jth chemical reaction in the chemical reaction network, and $\sigma = \sum_{j=1}^{r} \sigma_j$ the irreversible entropy creation already mentioned in (2.20). This shows that the total entropy creation is the sum of the creations of entropy of each chemical reaction in the chemical reaction network.

Remark 2.7. Comparing with the original irreversible port-Hamiltonian dynamics given by (2.12), the main common point is that the dynamics (2.14, or equivalently 2.21), maintains the skew-symmetric structure of the matrix $\mathcal{J}$ and uses the total internal energy U as the Hamiltonian function. The main difference is that there is one more dimension added to the state vector. In (2.12) the state vector is $x \in \mathbb{R}^m$, while in (2.14, or equivalently 2.21), the state vector is $z = [x, S] \in \mathbb{R}^{m+1}$. By adding the entropy S to the state vector, the variation of energy (or entropy) during the chemical reaction process, which is in line with the Gibbs' fundamental equation and follows the first and second laws of thermodynamics, can be expressed more clearly in the dynamical equation (2.14), or equivalently (2.21).

Remark 2.8. For a single chemical reaction, the irreversible port-Hamiltonian system given by (2.14), or equally in (2.21), takes the following formulation. In this case, C is an $m \times 1$ stoichiometric vector and $\mathcal{R}$ is a scalar. The dynamics become

$$\dot{z} = \mathcal{J}_{\mathcal{R}} \frac{\partial U}{\partial z} + g(z, \frac{\partial U}{\partial z}, u)$$

$$\text{with } \mathcal{J}_{\mathcal{R}} = \mathcal{R}\mathcal{J} = \begin{bmatrix} 0 & \cdots & 0 & \\ \vdots & \ddots & \vdots & C\mathcal{R} \\ 0 & \cdots & 0 & \\ -\mathcal{R}C^{tr} & & 0 & \end{bmatrix}.$$

2.4 Thermodynamic analysis

In this section, we apply the results of stability analysis to the irreversible port-Hamiltonian formulation given by (2.14) or (2.21), as described in Sect. 2.2. Note that in this section, only *isolated* chemical reaction networks are considered. That means that there is no mass or heat exchange between the chemical reaction network and external environment, i.e., in (2.14) or (2.21), $g(z, \frac{\partial U}{\partial z}(z), u) = 0$. Since the chemical reaction network is non-isothermal, the temperature $T \in \mathbb{R}_+$ is common to all chemical reactions in the network but not constant. Furthermore, the influence of volume and pressure will be neglected in this section.

2.4.1 Equilibrium for closed non-isothermal IPHS

First, we need to introduce the definition of equilibria, thermodynamic equilibria, and detailed balanced equations to the dynamics given by (2.14) or (2.21).

Definition 2.9. For an irreversible port-Hamiltonian system with dynamics given by (2.14) or (2.21), a vector z^* is called an equilibrium if $\dot{z}^* = Cv(z^*) = 0$, and a

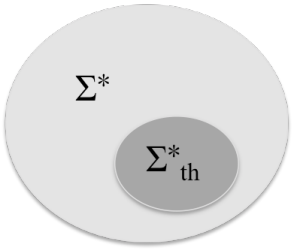

Figure 2.1: Set of equilibria Σ^* and set of thermodynamic equilibria Σ^*_{th}.

thermodynamic equilibrium if $v(z^*) = 0$, or equivalently $\mathcal{R}(z^*) = 0$. A chemical reaction network is called *detailed balanced* if it admits a thermodynamic equilibrium z^* satisfying $v(z^*) = 0$. The equations $v(z^*) = 0$ are called the detailed balanced equations.

Remark 2.10. Clearly, if z^* is a thermodynamic equilibrium, then z^* is an equilibrium. Let Σ^*_{th} be the set of thermodynamic equilibria and Σ^* be the set of equilibria. Thus $\Sigma^*_{th} \subseteq \Sigma^*$; see Figure 2.1. The converse inclusion holds if the stoichiometric matrix C is injective.

Let z^* be a thermodynamic equilibrium. Then, for a closed irreversible port-Hamiltonian system given by (2.14) or (2.21), $v(z^*) = 0$ means that, for $j = 1, \ldots, r$,

$$k_j^f \exp\left(Z_{\mathcal{S}_j}^{tr} \mathrm{Ln}(x^*) - \frac{E_j^f}{RT^*}\right) - k_j^b \exp\left(Z_{\mathcal{P}_j}^{tr} \mathrm{Ln}(x^*) - \frac{E_j^b}{RT^*}\right) = 0 \tag{2.22}$$

Assuming that $k_j^b \neq 0$, for $j = 1, \ldots, r$, we define the vectors $E^f \in \mathbb{R}^r$, $E^b \in \mathbb{R}^r$ and $K_{eq} \in \mathbb{R}^r$ as follows.

$$E^f = \begin{bmatrix} E_1^f \\ \vdots \\ E_r^f \end{bmatrix} \tag{2.23}$$

$$E^b = \begin{bmatrix} E_1^b \\ \vdots \\ E_r^b \end{bmatrix} \tag{2.24}$$

$$K_{eq} = \begin{bmatrix} K_{eq}^1 \\ \vdots \\ K_{eq}^r \end{bmatrix} = \begin{bmatrix} \frac{k_1^f}{k_1^b} \\ \vdots \\ \frac{k_r^f}{k_r^b} \end{bmatrix} \tag{2.25}$$

Then the equations (2.22), for $j = 1, \ldots, r$, are seen to be equivalent to

$$k_j^f \exp\left(Z_{\mathcal{S}_j}^{tr} \mathrm{Ln}(x^*) - \frac{E_j^f}{RT^*}\right) = k_j^b \exp\left(Z_{\mathcal{P}_j}^{tr} \mathrm{Ln}(x^*) - \frac{E_j^b}{RT^*}\right) \tag{2.26}$$

$$\frac{k_j^f}{k_j^b} = \exp[(Z_{\mathcal{P}_j}^{tr} - Z_{\mathcal{S}_j}^{tr})\mathrm{Ln}(x^*) + \frac{E_j^f - E_j^b}{RT^*}] \tag{2.27}$$

$$K_{eq}^j = \exp[(Z_{\mathcal{P}_j}^{tr} - Z_{\mathcal{S}_j}^{tr})\mathrm{Ln}(x^*) + \frac{E_j^f - E_j^b}{RT^*}] \tag{2.28}$$

Collecting all reactions in (2.28) and making use of the incidence matrix B of the complex graph, this can be rewritten as

$$K_{eq} = \mathrm{Exp}\left[C^{tr}\mathrm{Ln}(x^*) + \frac{1}{RT^*}(E^f - E^b)\right] \tag{2.29}$$

or

$$\mathrm{Ln}\, K_{eq} = C^{tr}\mathrm{Ln}(x^*) + \frac{1}{RT^*}(E^f - E^b) \tag{2.30}$$

For a chemical reaction network described in Sect. 2.2, the stoichiometric matrix C defined in (2.2) and (2.3), the vectors E^f, E^b and K_{eq} defined in (2.24), (2.23) and (2.25) are all constant, and R is the Boltzmann constant. Therefore, (2.30) constitutes a set of r linear equations in $m + 1$ variables (the m elements in the equilibrium concentration vector $x^* \in \mathbb{R}^m$ and the equilibrium temperature T^*). Assume that among the r equations, there are r' independent equations and $r' \leqslant r$. Clearly, for any chemical reaction network, we have $r' \leqslant m + 1$. If $r' = m + 1$, there is a unique thermodynamic equilibrium z^* at temperature T^*. If $r' < m + 1$, then there exists a set of thermodynamic equilibria at temperature T^* (denoted as Σ_{T^*}, see Proposition 2.13).

Proposition 2.11. *Consider an irreversible port-Hamiltonian system given by (2.21). Then for a given T^*, $z^* = [x^*, S^*]^{tr}$ is a thermodynamic equilibrium if and only if the concentration vector x^* and the entropy S^* satisfy*

$$\operatorname{Ln} K_{eq} - \frac{1}{RT^*}(E^f - E^b) = C^{tr} \operatorname{Ln}(x^*) \tag{2.31}$$

$$\frac{\partial U}{\partial S}|_{S=S^*} = T^* \tag{2.32}$$

Proof. We know that the stoichiometric matrix C, the vectors K_{eq}, E^f and E^b are all constant. For a certain equilibrium temperature T^*, the existence of $\operatorname{Ln}(x^*)$, $x^* \in \mathbb{R}^m_+$, satisfying (2.31) is obviously equivalent to (2.30). □

Remark 2.12. (2.31) and (2.32) show us the relations between the concentrations x, the entropy S and the temperature T at equilibrium. Equivalently, for a given S^*, $z^* = [x^*, S^*]^{tr}$ is a thermodynamic equilibrium if and only if the concentration vector x^* and the temperature T^* satisfy (2.31) and (2.32).

Proposition 2.13. *Let $z^* = [x^*, S^*]^{tr} \in \mathbb{R}^{m+1}$ be a thermodynamic equilibrium under a certain equilibrium temperature T^*, then the set of thermodynamic equilibria Σ_{T^*} is given as*

$$\Sigma_{T^*} := \{z^* \in \mathbb{R}^{m+1} \mid \operatorname{Ln} K_{eq} = C^{tr}\operatorname{Ln}(x^*) + \frac{1}{RT^*}(E^f - E^b), and \quad S^* = \frac{\partial U}{\partial T}(x^*, T^*)\} \tag{2.33}$$

Thus, once a thermodynamic equilibrium is given, the set of thermodynamic equilibria Σ_{T^*} is equal to

$$\Sigma_{T^*} := \{x^{**} \mid x^{**} \in \mathbb{R}^m_+, C^{tr}\operatorname{Ln}(x^{**}) = C^{tr}\operatorname{Ln}(x^*)\} \tag{2.34}$$

Furthermore, the set of all thermodynamic equilibria for different temperatures is given by

$$\Sigma^*_{th} = \bigcup_{T^*} \Sigma_{T^*} \tag{2.35}$$

Lemma 2.14. *If $T_1 \neq T_2$, then $\Sigma_{T_1} \cap \Sigma_{T_2} = \varnothing$*

Proof. If there exists a thermodynamic equilibrium $z^* = [x^*, S^*]^{tr} \in \Sigma_{T_1} \cap \Sigma_{T_2}$, then

$$\frac{1}{RT_1}(E^f - E^b) = \mathrm{Ln}\, K_{eq} - C^{tr}\mathrm{Ln}(x^*) \tag{2.36}$$

$$\frac{1}{RT_2}(E^f - E^b) = \mathrm{Ln}\, K_{eq} - C^{tr}\mathrm{Ln}(x^*) \tag{2.37}$$

Since the stoichiometric matrix C, the vectors K_{eq}, E^f and E^b are constant, and the R is constant, this implies

$$\frac{1}{T_1} = \frac{1}{T_2} \tag{2.38}$$

which means $T_1 = T_2$. □

2.4.2 Asymptotic stability

In this section, instead of using the total energy as generating function, see (Alonso and Ydstie 1996), (Alonso and Ydstie 2001), (Ydstie 2002), (Jillson and Ydstie 2007), (Hoang, Couenne, Jallut and Le Gorrec 2011) and (Hoang, Couenne, Jallut and Le Gorrec 2012), we use the internal energy to define an *energy based availability function* as the Lyapunov function candidate. We begin with some general properties of thermodynamic systems, see (Callen 2006), (Sandler et al. 2006), and show how this suggests a Lyapunov function.

The variation of the internal energy of a homogeneous system is defined by

$$dU = TdS - PdV + \sum_{i=1}^{m} \mu_i dn_i \tag{2.39}$$

where the extensive variables are the internal energy U, the entropy S, the volume V and the mole number vector $n \in \mathbb{R}^m_+$ with $n_i = x_i V, i = 1, ..., m$, and the intensive variables are the temperature T, the pressure P and the chemical potentials $\mu \in \mathbb{R}^m$ with μ_i the chemical potential of the ith species, $i = 1, \ldots, m$. Recall the expression of the Gibbs' free energy (Couenne et al. 2006)

$$G(T, P, n) = \sum_{i=1}^{m} n_i \mu_i \tag{2.40}$$

with

$$\begin{aligned}\mu_i &= \tilde{\mu_i}(P,T) + RT\ln(\tfrac{n_i}{\sum_{i=1}^{m} n_i}) \\ &= \tilde{h_i} - T\tilde{s_i} + RT\ln(\tfrac{n_i}{\sum_{i=1}^{m} n_i}) \\ &= c_{pi}(T - T_{ref}) + h_{iref} - T[c_{pi}\ln(\tfrac{T}{T_{ref}}) - R\ln(\tfrac{P}{P_{ref}}) + s_{iref}] + RT\ln(\tfrac{n_i}{\sum_{i=1}^{m} n_i})\end{aligned} \tag{2.41}$$

with the *heat capacities* c_{pi} of the ith species, a reference temperature T_{ref}, a molar reference enthalpy h_{iref}, a reference pressure P_{ref}, and a reference entropy s_{iref} of the ith species. Note that c_{pi}, T_{ref}, h_{iref}, P_{ref} and s_{iref} are constant.

Applying the Legendre transformation to (2.40), we obtain the following expression of the total internal energy

$$\begin{aligned}U(S,V,n) = \sum_{i=1}^{m} n_i[h_{iref} - c_{pi}T_{ref} + (c_{pi} - s_{iref} + c_{pi}\ln T_{ref} + R\ln\tfrac{\sum_{i=1}^{m} n_i R}{V} \\ + R\ln\tfrac{n_i}{\sum_{i=1}^{m} n_i})T(\xi) + (R - c_{pi})T(\xi)\ln T(\xi)] + (S - R\sum_{i=1}^{m} n_i)T(\xi)\end{aligned} \tag{2.42}$$

with $n = \sum_{i=1}^{m} n_i$ and

$$T(\xi) = T_{ref}\exp\left(\frac{\sum_{i=1}^{m} n_i[-s_{iref} + R\ln\frac{P}{P_{ref}} + R\ln\frac{n_i}{\sum_{i=1}^{m} n_i}] - S}{\sum_{i=1}^{m} n_i c_{pi}}\right) \tag{2.43}$$

We know, see (Callen 2006), (Alonso and Ydstie 2001), (Evans 2008) and (Jillson and Ydstie 2007), that for homogeneous systems, as a consequence of the second law of thermodynamics, the internal energy U is homogeneous of degree 1, and strictly convex with respect to the extensive variables. This allows us to define the positive definite availability function

$$A(\omega) = U(\omega) - U(\omega^*) - \frac{\partial^{tr}U}{\partial\omega}(\omega^*)\cdot(\omega - \omega^*) \tag{2.44}$$

with $\omega = (S, V, n)$.

Since in this chapter, the influence of the volume V and pressure P are not considered, we assume that $V = 1$ and $n_i = x_i V = x_i$, for $i = 1, \ldots, m$. Therefore, the internal energy $U(S, V, n)$ can be rewritten as $U(z)$ where $z = [x_1, \ldots, x_m, S]^{tr} \in \mathbb{R}^{m+1}$ is composed by concentrations x_i, $i = 1, ..., m$ and entropy S, which is the state vector for the dynamics of the irreversible port-Hamiltonian system (2.14).

Thus, the energy based availability function is defined as

$$A(z) = U(z) - U(z^*) - \frac{\partial^{tr} U}{\partial z}(z^*) \cdot (z - z^*) \tag{2.45}$$

with z^* a thermodynamic equilibrium at temperature T^*. Then the time-derivative of $A(z)$ equals

$$\frac{dA}{dt} = (\frac{\partial U}{\partial z}(z) - \frac{\partial U}{\partial z}(z^*))^{tr} \frac{dz}{dt} \tag{2.46}$$

This leads to the following proposition.

Proposition 2.15. *Consider a chemical reaction network represented by an irreversible port-Hamiltonian system given by (2.14) or (2.21). Let z^* be a thermodynamic equilibrium under a certain temperature T^*. Then z^* is asymptotically stable if the energy based availability function defined in (2.45) is a well-defined Lyapunov function. That means that the time-derivative of energy based availability function (2.46) is always less than or equal to zero, with strict equality only at z^*.*

More details about the asymptotic stability of IPHS will be discussed in the example in Sect. 2.5.

2.5 Example: a simple chemical reaction network

In this section, the results shown in this chapter will be illustrated on a simple chemical reaction network.

2.5.1 IPHS Modelling

Consider the following simple non-isothermal reaction network at constant volume $V = 1$, with an input flow $f_s^e = \lambda_e(1 - \frac{T}{T_e})$ which corresponds to the heat transfer from the outside of the reactor, with a constant thermal conductivity $\lambda_e \in \mathbb{R}_+$, and a constant reference temperature $T_e \in \mathbb{R}_+$

$$X_1 + 2X_2 \underset{k_1^b}{\overset{k_1^f}{\rightleftharpoons}} X_3$$
$$X_3 \underset{k_2^b}{\overset{k_2^f}{\rightleftharpoons}} 2X_1 + X_2$$

The influence of the volume V and pressure P is not considered in this example. The temperature $T \in \mathbb{R}_+$ is common to all chemical reactions in the network but not constant. In this chemical reaction network, since there are 2 chemical reactions, 3 chemical species and 3 complexes, $m = 3$, $r = 2$, $c = 3$. We denote the state vector by $z = [x_1, x_2, x_3, S]^{tr} \in \mathbb{R}^4$, with the concentrations of ith species x_i, $i = 1, 2, 3$, and the entropy of system S. The Hamiltonian function H equals the total internal energy U, and the co-state vector $\frac{\partial U}{\partial z} = [\mu_1, \mu_2, \mu_3, T]^{tr} \in \mathbb{R}^4$ consists of the chemical potentials of ith species μ_i, $i = 1, 2, 3$, and the temperature T. The stoichiometric matrix $C \in \mathbb{R}^{3\times 2}$ is given as

$$C = \begin{bmatrix} -1 & 2 \\ -2 & 1 \\ 1 & -1 \end{bmatrix},$$

the complex composition matrix $Z \in \mathbb{R}^{3\times 3}$ is given as

$$Z = \begin{bmatrix} 1 & 0 & 2 \\ 2 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix},$$

and the incidence matrix $B \in \mathbb{R}^{3\times 2}$ is given as

$$B = \begin{bmatrix} -1 & 0 \\ 1 & -1 \\ 0 & 1 \end{bmatrix}$$

For the first chemical reaction, $j = 1$, the constant skew-symmetric matrix $\mathcal{J}_1 \in \mathbb{R}^{4\times 4}$ can be written as

$$\mathcal{J}_1 = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 2 \\ 0 & 0 & 0 & -1 \\ -1 & -2 & 1 & 0 \end{bmatrix}$$

and for the chemical second reaction, $j = 2$, the constant skew-symmetric matrix $\mathcal{J}_2 \in \mathbb{R}^{4\times 4}$ equals

$$\mathcal{J}_2 = \begin{bmatrix} 0 & 0 & 0 & -2 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 \\ 2 & 1 & -1 & 0 \end{bmatrix}$$

According to the expression of $\mathcal{J}_{\mathcal{R}}$ in (2.18), we have

$$\begin{aligned} \mathcal{J}_{\mathcal{R}} &= \sum_{j=1}^{2} \mathcal{R}_j(z, \tfrac{\partial U}{\partial z}, \tfrac{\partial S}{\partial z})\mathcal{J}_j \\ &= \begin{bmatrix} 0 & 0 & 0 & -\mathcal{R}_1 + 2\mathcal{R}_2 \\ 0 & 0 & 0 & -2\mathcal{R}_1 - \mathcal{R}_2 \\ 0 & 0 & 0 & -\mathcal{R}_2 + \mathcal{R}_1 \\ \mathcal{R}_1 - 2\mathcal{R}_2 & 2\mathcal{R}_1 + \mathcal{R}_2 & \mathcal{R}_2 - R_1 & 0 \end{bmatrix} \end{aligned}$$

where $\mathcal{R} = [\mathcal{R}_1, \mathcal{R}_2]^{tr} = \left[(\frac{v_1}{T\mathcal{A}_1})\mathcal{A}_1, (\frac{v_2}{T\mathcal{A}_2})\mathcal{A}_2\right]^{tr}$, with the reaction rate of the first chemical reaction v_1 and of the second chemical reaction v_2, the chemical affinity of the first chemical reaction $\mathcal{A}_1$ and of the second chemical reaction $\mathcal{A}_2$.

For the first chemical reaction, $j = 1$, we have

$$\mathcal{A}_1 = -\sum_{i}^{3} C_{i1}\mu_i = \mu_1 + 2\mu_2 - \mu_3$$

$$v_1 = k_1^f \exp\left(\begin{bmatrix} 1 & 2 & 0 \end{bmatrix} \cdot \mathrm{Ln}(x) - \frac{E_1^f}{RT}\right) - k_1^b \exp\left(\begin{bmatrix} 0 & 0 & 1 \end{bmatrix} \mathrm{Ln}(x) - \frac{E_1^b}{RT}\right)$$

where k_1^f, k_1^f, E_1^f, E_1^b are constant. For the second chemical reaction, $j = 2$, we obtain

$$\mathcal{A}_3 = -\sum_{i}^{m} C_{i2}\mu_i = -2\mu_1 - \mu_2 + \mu_3$$

$$v_2 = k_2^f \exp\left(\begin{bmatrix} 0 & 0 & 1 \end{bmatrix} \cdot \mathrm{Ln}(x) - \frac{E_2^f}{RT}\right) - k_2^b \exp\left(\begin{bmatrix} 2 & 1 & 0 \end{bmatrix} \mathrm{Ln}(x) - \frac{E_2^b}{RT}\right)$$

where k_2^f, k_2^f, E_2^f, E_2^b are constant. For the input of system, the function $g(z, \frac{\partial U}{\partial z}, u)$ is given by

$$g(z, \frac{\partial U}{\partial z}, u) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} f_s^e = \lambda_e(1 - \frac{T}{T_e}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

Finally we obtain the irreversible port-Hamiltonian formulation of this chemical reaction network as

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \\ \dot{S} \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & -\mathcal{R}_1 + 2\mathcal{R}_2 \\ 0 & 0 & 0 & -2\mathcal{R}_1 - \mathcal{R}_2 \\ 0 & 0 & 0 & -\mathcal{R}_2 + \mathcal{R}_1 \\ \mathcal{R}_1 - 2\mathcal{R}_2 & 2\mathcal{R}_1 + \mathcal{R}_2 & -\mathcal{R}_1 + \mathcal{R}_2 & 0 \end{bmatrix} \begin{bmatrix} \mu_1 \\ \mu_2 \\ \mu_3 \\ T \end{bmatrix} + \lambda_e(1 - \frac{T}{T_e}) \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \tag{2.47}$$

2.5.2 Equilibrium analysis

At a thermodynamic equilibrium point $z^* = [x^*, S^*]^{tr}$, we have $v = [v_1, v_2]^{tr} = 0$ and $\mathcal{R} = [\mathcal{R}_1, \mathcal{R}_2]^{tr} = 0$. Based on the equations (2.16), (2.17), (2.18), we infer that

$$k_1^f \exp\left(Z_{\mathcal{S}_1}^{tr} \mathrm{Ln}(x^*) - \frac{E_1^f}{RT^*}\right) - k_1^b \exp\left(Z_{\mathcal{P}_1}^{tr} \mathrm{Ln}(x^*) - \frac{E_1^b}{RT^*}\right) = 0 \tag{2.48}$$

$$k_2^f \exp\left(Z_{\mathcal{S}_2}^{tr} \mathrm{Ln}(x^*) - \frac{E_2^f}{RT^*}\right) - k_2^b \exp\left(Z_{\mathcal{P}_2}^{tr} \mathrm{Ln}(x^*) - \frac{E_2^b}{RT^*}\right) = 0 \tag{2.49}$$

We define the matrix E^f, E^b and K_{eq} as (2.23), (2.24), (2.25):

$$E^f = \begin{bmatrix} E_1^f \\ E_2^f \end{bmatrix} \tag{2.50}$$

$$E^b = \begin{bmatrix} E_1^b \\ E_2^b \end{bmatrix} \tag{2.51}$$

$$\begin{aligned} K_{eq} &= \begin{bmatrix} K_{eq}^1 \\ K_{eq}^2 \end{bmatrix} = \begin{bmatrix} \frac{k_1^f}{k_1^b} \\ \frac{k_2^f}{k_2^b} \end{bmatrix} \\ &= \begin{bmatrix} \exp\left((Z_{\mathcal{P}_1}^{tr} - Z_{\mathcal{S}_1}^{tr})\mathrm{Ln}(x^*) + \frac{E_1^f}{RT^*} - \frac{E_1^b}{RT^*}\right) \\ \exp\left((Z_{\mathcal{P}_2}^{tr} - Z_{\mathcal{S}_2}^{tr})\mathrm{Ln}(x^*) + \frac{E_2^f}{RT^*} - \frac{E_2^b}{RT^*}\right) \end{bmatrix} \\ &= \mathrm{Exp}\left[C^{tr}\mathrm{Ln}(x^*) + \tfrac{1}{RT^*}(E^f - E^b)\right] \end{aligned} \tag{2.52}$$

This leads to

$$\mathrm{Ln}\, K_{eq} = C^{tr}\mathrm{Ln}(x^*) + \frac{1}{RT^*}(E^f - E^b) \tag{2.53}$$

Since $m = 3$ and $r = 2$, $m + 1 = 4$ and $r' \leqslant r = 2$. Therefore, we deduce that $r' < m + 1$, and thus there exists a set of thermodynamic equilibria Σ_{T^*} at temperature T^*. Expanding the equation (2.53), we obtain

$$\ln K_{eq}^1 = -\ln x_1^* - 2\ln x_2^* + \ln x_3^* + \frac{E_1^f - E_1^b}{RT^*}$$

$$\ln K_{eq}^2 = 2\ln x_1^* + \ln x_2^* - \ln x_3^* + \frac{E_2^f - E_2^b}{RT^*}$$

Hence, the set of thermodynamic equilibria Σ_{T^*} under the temperature T^* can be written as

$$\Sigma_{T^*} = \left\{ z^* \in \mathbb{R}^4 \mid z^* = [x^*, S^*]^{tr}, S^* = \frac{\partial U}{\partial T}(T^*) \in \mathbb{R}, x^* \in \mathbb{R}^3 \right\} \tag{2.54}$$

where $x^* = \left[\frac{k_1^f k_2^f x_2^*}{k_1^b k_2^b \exp\left(\frac{E_1^f + E_2^f - E_1^b - E_2^b}{RT^*}\right)}, x_2^*, \frac{(k_1^f)^2 k_2^f x_2^*}{(k_1^b)^2 k_2^b \exp\left(\frac{2E_1^f + E_2^f - 2E_1^b - E_2^b}{RT^*}\right)} \right]^{tr}$, with $x_2^* \in \mathbb{R}$.

2.5.3 Asymptotic stability

We will check if the availability function $A(z)$ defines a valid Lyapunov function. Clearly, we have $A(z^*) = 0$. In addition, because of the strict convexity of the internal energy $U(z)$, it is easy to prove that also $A(z)$ is convex, showing that A has a minimum at z^*. Finally, we have

$$\begin{aligned}
&\tfrac{dA}{dt} = \tfrac{dU}{dz} \cdot \tfrac{dz}{dt} \\
&= \left(\tfrac{\partial U}{\partial z}(z) - \tfrac{\partial U}{\partial z}(z^*)\right)^{tr} \cdot \tfrac{dz}{dt} \\
&= \left(\tfrac{\partial U}{\partial z}(z) - \tfrac{\partial U}{\partial z}(z^*)\right)^{tr} \left[(\mathcal{R}_1\mathcal{J}_1 + \mathcal{R}_2\mathcal{J}_2)\tfrac{\partial U}{\partial z}(z) + g(z, \tfrac{\partial U}{\partial z}, u)\right] \\
&= -\tfrac{\partial U}{\partial z}(z^*)(\mathcal{R}_1\mathcal{J}_1 + \mathcal{R}_2\mathcal{J}_2)\tfrac{\partial U}{\partial z}(z) + \left(\tfrac{\partial U}{\partial z}(z) - \tfrac{\partial U}{\partial z}(z^*)\right)^{tr} g(z, \tfrac{\partial U}{\partial z}, u)
\end{aligned}$$

By using (2.13) and due to the fact that $\{S, U\}_{\mathcal{J}_j} = \mathcal{A}_j$, $j = 1, 2$, and $\tfrac{\partial U}{\partial z}(z^*)\mathcal{J}_j\tfrac{\partial U}{\partial z}(z) = -T\mathcal{A}_j^* + T^*\mathcal{A}_j$, $j = 1, 2$, the time-derivative of $A(z)$ equals

$$\begin{aligned}
\tfrac{dA}{dt} = \quad & -\gamma_1 \tfrac{\partial U}{\partial z}(z^*)\mathcal{J}_1\tfrac{\partial U}{\partial z}(z)\{S, U\}_{\mathcal{J}_1} - \gamma_2 \tfrac{\partial U}{\partial z}(z^*)\mathcal{J}_2\tfrac{\partial U}{\partial z}(z)\{S, U\}_{\mathcal{J}_2} \\
& + \left(\tfrac{\partial U}{\partial z}(z) - \tfrac{\partial U}{\partial z}(z^*)\right)^{tr} g(z, \tfrac{\partial U}{\partial z}, u) \\
& = \gamma_1 T\mathcal{A}_1^*\mathcal{A}_1 - \gamma_1 T^*\mathcal{A}_1^2 + \gamma_2 T\mathcal{A}_2^*\mathcal{A}_2 - \gamma_2 T^*\mathcal{A}_2^2 + \lambda_e(T - T^*)(1 - \tfrac{T}{T_e})
\end{aligned} \tag{2.55}$$

Because at a thermodynamic equilibrium point, we have $\mathcal{A}_1^* = \mathcal{A}_2^* = 0$, we thus obtain

$$\frac{dA}{dt} = -\gamma_1 T^*\mathcal{A}_1^2 - \gamma_2 T^*\mathcal{A}_2^2 + \lambda_e(T - T^*)(1 - \frac{T}{T_e})$$

Since the first term $-\gamma_1 T^*\mathcal{A}_1^2$ and the second term $-\gamma_2 T^*\mathcal{A}_2^2$ are always negative and vanish at the equilibrium point, it remains to select a certain temperature T such that the third term becomes negative and vanishes at the equilibrium point. Expanding the third term, we obtain

$$\lambda_e(T - T^*)(1 - \frac{T}{T_e}) = \frac{\lambda_e}{T_e}\left[-T^2 + (T_e + T^*)T - T^*T_e\right]$$

Hence, we obtain the following condition for asymptotic stability of the equilibrium temperature

$$T^* = T_e \tag{2.56}$$

(2.56) shows that at $T = T_e$, the irreversible port-Hamiltonian system given in (2.14) or (2.21) representing the chemical reaction network described in Sect. 2.2, is asymptotically stable around the thermodynamic equilibrium point, in accordance with Propostion 2.15. Moreover, according to (2.54), the set of thermodynamic equilibria $\Sigma_{T*=T_e}$ can be written as

$$\Sigma_{T_e} = \left\{ \begin{array}{l} z^* \in \mathbb{R}^4 \mid z^* = [x^*, S^*]^{tr}, S^* = \frac{\partial U}{\partial T}(T_e) \in \mathbb{R}, x_2^* \in \mathbb{R} \\ \\ and \quad x^* = \left[\frac{k_1^f k_2^f x_2^*}{k_1^b k_2^b \exp\left(\frac{E_1^f + E_2^f - E_1^b - E_2^b}{RT_e}\right)}, x_2^*, \frac{(k_1^f)^2 k_2^f x_2^*}{(k_1^b)^2 k_2^b \exp\left(\frac{2E_1^f + E_2^f - 2E_1^b - E_2^b}{RT_e}\right)} \right]^{tr} \end{array} \right\}$$

2.6 Conclusion

In this chapter, an irreversible port-Hamiltonian formulation, generated by the internal energy, has been given for non-isothermal mass action kinetics chemical reaction networks. This port-Hamiltonian formulation allowed us to analyze the set of thermodynamic equilibria and the asymptotic stability of non-isothermal chemical reaction networks. These results have been illustrated on a simple non-isothermal chemical reaction network.

Chapter 3

Quasi port-Hamiltonian formulation generated by the total entropy

3.1 Introduction

Modeling of chemical reaction networks has attracted much attention in the last decades due to its wide application in systems biology and chemical engineering. Previous work, such as (Horn and Jackson 1972), (Horn 1972) and (Feinberg 1972), provides the foundation of a structural theory of isothermal chemical reaction networks governed by *mass action kinetics*. From then on, a series of papers about the modeling and analysis of mass action kinetics chemical reaction networks appeared, given in (Rao et al. 2014), (Jayawardhana et al. 2012), (Balabanian and Bickart 1981), (Varma and Palsson 1994). In most of these papers, the chemical reactions are assumed to take place under *isothermal* condition. Consequently, the influence of in/outflow of heat can not be taken into account. Hence, non-isothermal chemical reaction networks still pose fundamental challenges.

In this chapter, we aim to use the port-Hamiltonian framework for the modeling of non-isothermal mass action kinetics chemical reaction networks. Port-Hamiltonian systems theory (PHS) has been intensively employed in the modeling and passivity-based control of electrical, mechanical and electromechanical systems, given in (Maschke and van der Schaft 1991), (van der Schaft and Maschke 1995) and (van der Schaft 2006). In (van der Schaft et al. 2013a) and (van der Schaft et al. 2013b), a port-Hamiltonian formulation of isothermal mass action kinetics chemical reaction networks was provided.

A first step to non-isothermal chemical reaction networks was taken in the previous chapter. Based on the previous works (Eberard et al. 2007), (Favache et al. 2009), (Ramırez, Le Gorrec, Maschke and Couenne 2013) and (Ramirez, Maschke and Sbarbaro 2013b), a new quasi port-Hamiltonian formulation for non-isothermal chemical reaction networks will be developed in this chapter. Comparing with the IPHS in the previous chapter, this quasi port-Hamiltonian formulation is generated

by the total entropy instead of the internal energy. Thus, not only the energy balance equations but also the entropy balance equations will be used in this new port-Hamiltonian formulation.

The main contributions of the present chapter are as follows. First, based on mass and energy balance equations, a port-Hamiltonian formulation for non-isothermal mass action kinetics chemical reaction networks which are detailed balanced is developed. This formulation directly extends the port-Hamiltonian formulation of isothermal chemical reaction networks of (van der Schaft et al. 2013a) and (van der Schaft et al. 2013b), in contrast with the irreversible port-Hamiltonian formulation given in the previous chapter. It exhibits the energy balance and the thermodynamic principles in an explicit way. Based on the obtained port-Hamiltonian formulation, we provide a thermodynamic analysis of the existence and characterization of thermodynamic equilibria and their asymptotic stability. For the asymptotic stability, a comparable statement with the one in (Rao and Esposito 2016) is found. Being directly related with the energy and entropy functions, this port-Hamiltonian formulation is easily applicable to chemical and biological systems. The second contribution of this chapter is the extension of the port-Hamiltonian formulation and the thermodynamic analysis to non-isothermal chemical reaction networks with external ports.

The structure of the chapter is as follows. Sect. 3.2 develops the port-Hamiltonian formulation of non-isothermal chemical reaction networks, and shows how this formulation is in line with the main laws of thermodynamics. In Sect. 3.3, a thermodynamic analysis will be carried out, including the characterization of equilibria and their asymptotic stability. An example, namely a genetic protein synthesis circuit with internal feedback and cell-to-cell communication, is discussed as an illustration of the developed theory. Sect. 3.4 extends the previous results to non-isothermal chemical reaction networks with external ports.

3.2 Modeling

In this section, we will develop a new quasi port-Hamiltonian formulation based on entropy balance equations, for detailed balanced mass action kinetics chemical reaction networks, see (Temkin et al. 1996), (Feinberg 1989), (Rao et al. 2013). We will use the basic notions of chemical reaction networks as introduced in Sect. 2.2.

First, we assume that in the chemical reaction network, the equilibration following any reaction event is much faster than any reaction time scale. Thus, all intensive thermodynamic variables are well defined and equal everywhere in the system. Then, we assume that the chemical reaction network is closed and under-

goes an adiabatic process. That means there is no heat or mass transfer between the system and the external environment. Moreover, the chemical reaction network is isochoric so that volume change can be neglected, i.e. $dV = 0$.

As opposed to the irreversible port-Hamiltonian formulation generated by the internal energy in Sect. 2.3, the thermodynamic equilibrium will be discussed for the dynamical equations of this new quasi port-Hamiltonian system. Since the state vector will be different as well, we start by rewriting the definition of thermodynamic equilibrium for non-isothermal isothermal chemical reaction networks, extending the definitions for isothermal chemical reaction networks, given in e.g. (van der Schaft et al. 2013a).

Definition 3.1. A vector of concentrations x^* is called an *equilibrium* for the dynamics $\dot{x} = Cv(x, T)$ for a certain temperature T if $Cv(x^*, T) = 0$, and a *thermodynamic equilibrium* if $v(x^*, T) = 0$. A chemical reaction network $\dot{x} = Cv(x, T)$ is called detailed-balanced if it admits a thermodynamic equilibrium for every temperature T.

In order to stress the dependence on T, the thermodynamical equilibrium will be denoted by $x^*(T)$. The conditions for existence of a thermodynamic equilibrium will be discussed in Sect. 3.3.1. Throughout this section we assume that there exists at least one thermodynamic equilibrium, like in the isothermal case, see e.g. (van der Schaft et al. 2013a) and (van der Schaft et al. 2013b) . Thus we throughout assume that the network is detailed-balanced. We will use the existence of this thermodynamic equilibrium to develop the new quasi port-Hamiltonian formulation.

3.2.1 Mass balance equations

Let us recall the mass balance equations of a detailed balanced reaction network according to (van der Schaft et al. 2013a). Let $x^*(T) \in \mathbb{R}^m_+$ be a thermodynamic equilibrium for a certain temperature T, i.e.,

$$v(x^*(T), T) = 0 \tag{3.1}$$

Then we define the *conductance* $\kappa_j(T)$ of the jth reaction as:

$$\kappa_j(T) := k^f_j \mathrm{Exp}(Z^{tr}_{\mathcal{S}_j} \ln(x^*(T)) - \frac{E^f_j}{RT}) = k^b_j \mathrm{Exp}(Z^{tr}_{\mathcal{P}_j} \ln(x^*(T)) - \frac{E^b_j}{RT}) \tag{3.2}$$

Furthermore the reaction rate of the jth chemical reaction (2.8) can be rewritten as

$$\begin{aligned} v_j(x,T) &= k_j^f \exp(Z_{S_j}^{tr}\mathrm{Ln}(x) - \tfrac{E_j^f}{RT}) - k_j^b \exp(Z_{P_j}^{tr}\mathrm{Ln}(x) - \tfrac{E_j^b}{RT}) \\ &= \kappa_j(T)[\exp(Z_{\mathcal{S}_j}^{tr}\mathrm{Ln}(\tfrac{x}{x^*(T)})) - \exp(Z_{\mathcal{P}_j}^{tr}\mathrm{Ln}(\tfrac{x}{x^*(T)}))] \end{aligned} \tag{3.3}$$

Now define the $r \times r$ diagonal matrix of conductances $K(T)$ as

$$K(T) := \mathrm{diag}(\kappa_1(T), \ldots, \kappa_r(T)) \tag{3.4}$$

Collecting all the reaction rates in (3.3) and employing the incidence matrix B defined in Sect. 2.2, the chemical reaction rate vector of a detailed balanced non-isothermal reaction network can be written as

$$v(x,T) = -K(T)B^{tr}\mathrm{Exp}(Z^{tr}\mathrm{Ln}(\frac{x}{x^*(T)})) \tag{3.5}$$

Hence the dynamics of a detailed balanced mass action kinetics reaction network can be expanded as

$$\begin{aligned} \dot{x} &= Cv(x,T) \\ &= -ZBK(T)B^{tr}\mathrm{Exp}(Z^{tr}\mathrm{Ln}(\tfrac{x}{x^*(T)})) \\ &= -ZBK(T)B^{tr}\mathrm{Exp}(\tfrac{Z^{tr}\mu}{RT}) \\ &= -ZL\mathrm{Exp}(\tfrac{Z^{tr}\mu}{RT}) \end{aligned} \tag{3.6}$$

where $\mu = RT\mathrm{Ln}(\frac{x}{x^*(T)})$ is the vector of *chemical potentials* and $L := BK(T)B^{tr}$ is the weighted Laplacian matrix for the reaction network graph, with weights given by the conductances $\kappa_1(T), \ldots, \kappa_r(T)$.

Note that the value of the conductances $\kappa_1(T), \ldots, \kappa_r(T)$ not only depends on the temperature T, but also on the choice of the thermodynamic equilibrium $x^*(T)$. However, if the reaction network graph is connected, then for any other thermodynamical equilibrium $x^{**}(T)$ for the same temperature T, there exists a positive constant c_0 such that

$$K(x^{**}(T),T) = c_0 K(x^*(T),T) \tag{3.7}$$

$$\mathrm{Exp}\,(Z^{tr}\mathrm{Ln}(\frac{x}{x^{**}(T)})) = \frac{1}{c_0}\mathrm{Exp}\,(Z^{tr}\mathrm{Ln}(\frac{x}{x^{*}(T)})) \tag{3.8}$$

This property of the matrix K has been proved in (van der Schaft et al. 2013a). It implies that the dependence on $x^*(T)$ is minor; choosing another thermodynamical equilibrium only involves a uniform scaling of K, and thus of L. Another well-known property of L is the fact that the matrix L is independent of the orientation of the graph (Bollobas 1998).

3.2.2 Energy balance equations

In this section we will express the energy conservation for a closed chemical reaction network in order to encompass the thermodynamic properties of the system.

Assuming that in the system the variation of the volume may be neglected, i.e. $dV = 0$, Gibbs' relation reduces to

$$dU = \mu^{tr} dx + T dS \tag{3.9}$$

where U denotes the internal energy, S the entropy, and the conjugated intensive variables are the chemical potential $\frac{\partial U}{\partial x} = \mu$ and the temperature $\frac{\partial U}{\partial S} = T$. This implies

$$\frac{dU}{dt} = \mu^{tr}\frac{dx}{dt} + T\frac{dS}{dt} \tag{3.10}$$

Using the equation (3.6), the first term on the right-hand side of (3.10) also equals

$$\mu^{tr}\frac{dx}{dt} = -\mu^{tr} Z L \mathrm{Exp}(\frac{Z^{tr}\mu}{RT}) \tag{3.11}$$

Since the system is considered to be isolated, the energy balance equation is

$$\frac{dU}{dt} = 0 \tag{3.12}$$

This implies that the second term in (3.11) equals

$$T\frac{dS}{dt} = \mu^{tr} Z L \mathrm{Exp}(\frac{Z^{tr}\mu}{RT}) \tag{3.13}$$

In the next section we will combine these equations with (3.6) in order to derive a port-Hamiltonian formulation of non-isothermal and isolated reaction networks.

3.2.3 Port-Hamiltonian formulation

In this section, we show how Sect. 3.2.1 and Sect. 3.2.2 can be combined into a port-Hamiltonian formulation of the dynamics of detailed balanced chemical reaction networks.

Firstly, we define the state vector $z = [x^{tr}, U]^{tr} = [x_1, \dots, x_m, U]^{tr}$, where x is the vector of concentrations and U the internal energy. Then we define the Hamiltonian function $\mathrm{H} = -S$, where S is the entropy. Note that the Gibbs' relation (3.9) can also be written in the entropy formulation

$$dS = \sum_{i=1}^{m} (\frac{dS}{dx_i})^{tr} dx_i + \frac{dS}{dU} dU,$$

where $\frac{dS}{dx_i} = -\frac{\mu_i}{T}$ and $\frac{dS}{dU} = \frac{1}{T}$ are the intensive thermodynamic variables conjugated to x_i and the internal energy U. This implies that the co-state vector corresponding to $\mathrm{H} = -S$ is

$$\frac{\partial \mathrm{H}}{\partial z} = \frac{\partial(-S)}{\partial z} = \begin{bmatrix} \frac{\mu_1}{T} & \dots & \frac{\mu_m}{T} & -\frac{1}{T} \end{bmatrix}^{tr} \tag{3.14}$$

Note that μ and T can be expressed as function of the components of this co-state vector. Now define the skew-symmetric matrix

$$\mathcal{J}(\frac{\partial \mathrm{H}}{\partial z}(z)) := \begin{bmatrix} 0 & \cdots & 0 & \\ \vdots & \ddots & \vdots & TZL\mathrm{Exp}(\frac{Z^{tr}\mu}{RT}) \\ 0 & \cdots & 0 & \\ -T(ZL\mathrm{Exp}(\frac{Z^{tr}\mu}{RT}))^{tr} & & 0 & \end{bmatrix} \tag{3.15}$$

and the symmetric matrix

$$\mathcal{R}(\frac{\partial \mathrm{H}}{\partial z}(z)) := \begin{bmatrix} 0 & \cdots & 0 & \\ \vdots & \ddots & \vdots & \mathbf{0}_m \\ 0 & \cdots & 0 & \\ (\mathbf{0}_m)^{tr} & & T\mu^{tr}ZL\mathrm{Exp}(\frac{Z^{tr}\mu}{RT}) & \end{bmatrix} \tag{3.16}$$

It follows that the dynamics of the non-isothermal mass action kinetics chemical reaction network (2.1) given by the mass balance equation (3.6) and the energy balance equation (3.12), can be written into quasi port-Hamiltonian form

$$\dot{z} = (\mathcal{J}(\frac{\partial \mathrm{H}}{\partial z}(z)) - \mathcal{R}(\frac{\partial \mathrm{H}}{\partial z}(z)))\frac{\partial \mathrm{H}}{\partial z}(z) \tag{3.17}$$

As we will see in Sect. 3.2.4, $T\mu^{tr}ZL\mathrm{Exp}(\frac{Z^{tr}\mu}{RT}) \geqslant 0$ and thus R is positive semi-definite. The formulation (3.17) is called 'quasi port-Hamiltonian', since the structure matrices $\mathcal{J}$ and $\mathcal{R}$ depend on the co-state variables,

$$\frac{\partial \mathrm{H}}{\partial z} = \frac{\partial(-S)}{\partial z} = \left[\frac{\mu_1}{T}, \ldots, \frac{\mu_m}{T}, -\frac{1}{T}\right]^{tr}$$

instead of only on the state variables $[x_1, \ldots, x_m, U]^{tr}$ as in the irreversible port-Hamiltonian formulation in (2.21) in Sect. 2.3. This formulation is comparable to the formulation of the mass balance and energy balance equations such as GENERIC, suggested, see (Jongschaap and Öttinger 2004), or the port-Hamiltonian formulation with generating function being the availability function derived from the entropy function, see (Hoang, Couenne, Jallut and Gorrec 2011).

3.2.4 Entropy balance equation

In this section, we shall relate the positive semi-definiteness of the dissipation matrix $\mathcal{R}$ in (3.16) with the second law of thermodynamics. With this in mind let us compute the time-derivative of the entropy S

$$\begin{aligned}
\tfrac{dS}{dt} &= \tfrac{\partial^{tr} S(z)}{\partial z}\dot{z} \\
&= \tfrac{\partial^{tr} S(z)}{\partial z}(\mathcal{J}(\tfrac{\partial \mathrm{H}}{\partial z}(z)) - \mathcal{R}(\tfrac{\partial \mathrm{H}}{\partial z}(z)))\tfrac{\partial \mathrm{H}}{\partial z}(z) \\
&= [-\tfrac{\mu^{tr}}{T}\tfrac{1}{T}]\begin{bmatrix} \mathbf{0}_{m\times m} & TZL\mathrm{Exp}(\frac{Z^{tr}\mu}{RT}) \\ -T(ZL\mathrm{Exp}(\frac{Z^{tr}\mu}{RT}))^{tr} & -T\mu^{tr}ZL\mathrm{Exp}(\frac{Z^{tr}\mu}{RT}) \end{bmatrix}\begin{bmatrix} \frac{\mu}{T} \\ -\frac{1}{T} \end{bmatrix} \\
&= \tfrac{1}{T}\mu^{tr}ZL\mathrm{Exp}(\tfrac{Z^{tr}\mu}{RT})
\end{aligned} \tag{3.18}$$

Denote $\gamma = \frac{Z^{tr}\mu}{RT}$. It has been shown in (van der Schaft et al. 2013a) (using the properties of the Laplacian matrix L) that for any $\gamma \in \mathbb{R}^c$,

$$\gamma^{tr}L\mathrm{Exp}(\gamma) \geqslant 0, \tag{3.19}$$

while $\gamma^{tr}L\mathrm{Exp}(\gamma) = 0$ if and only if $B^{tr}\gamma = 0$. Hence, the entropy balance equation (3.18) becomes

$$\frac{dS}{dt} = R\gamma^{tr}L\mathrm{Exp}(\gamma) =: \sigma \geqslant 0 \tag{3.20}$$

Here σ is the irreversible entropy source term. Note that in equation (3.20), the time-derivative of the entropy S is deduced from the port-Hamiltonian formulation (3.17) defined in Sect. 3.2.3. It is consistent with equation (3.13), which is deduced from the Gibbs' relation (3.9).

Furthermore, note that the positivity of the irreversible entropy source term is equivalent to the positive semi-definiteness of the dissipation matrix $\mathcal{R}(\frac{\partial \mathrm{H}}{\partial z}(z))$ in (3.16). Indeed the only non-zero term of $\mathcal{R}(\frac{\partial \mathrm{H}}{\partial z}(z))$ is the $(m+1, m+1)$th element, denoted as $\mathcal{R}_{m+1,m+1}$, which is related to the entropy source term as

$$\mathcal{R}_{m+1,m+1} = \sigma T^2 \tag{3.21}$$

In summary, the quasi port-Hamiltonian representation of chemical reaction networks given in (3.15), (3.16) and (3.17) represents the mass and energy balance equations. Moreover from its structure, it implies the entropy balance equation. It differs from the expression of energy and entropy balance equations, see (Qian and Beard 2005), which are expressed for non-equilibrium biochemical systems. It differs from the expression in (Rao and Esposito 2016), where the free energy and entropy balance are considered in an isothermal case when the species are diluted in a solvent, which acts as a thermal bath, while the pressure P is set by the environment. It differs also from the irreversible port-Hamiltonian representation of the mass and entropy balance equations of chemical reaction networks in (Ramirez et al. 2014) and (Wang et al. 2016), which is introduced in the previous chapter, by the fact that it is based on the energy balance equation instead of on the entropy balance equation. Note that the description based on the energy balance equation is classical (Favache et al. 2010), and more easily derived than the description based on the entropy balance equation. Moreover, the quasi port-Hamiltonian formulation given in (3.15), (3.16) and (3.17) fundamentally differs from the representation of chemical reaction networks as port Hamiltonian systems in (Otero-Muras et al. 2008) as well, by the fact that this quasi port-Hamiltonian representation is established on the whole space of concentration vectors instead of only locally around an equilibrium point, as in (Otero-Muras et al. 2008).

Finally this quasi port-Hamiltonian directly extends the port-Hamiltonian formulation of isothermal chemical reaction networks obtained in (van der Schaft et al. 2013a) and (van der Schaft et al. 2013b) by adding the energy balance equation to the dynamical equations.

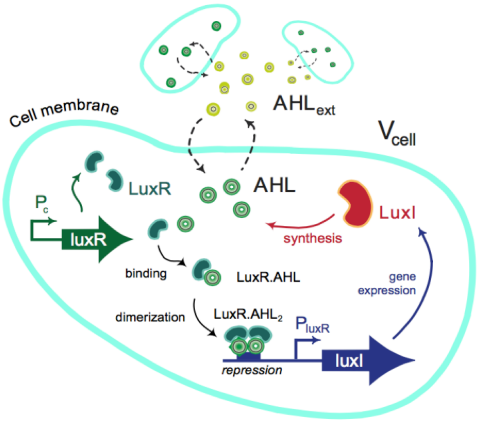

Figure 3.1: Synthetic gene circuit.

3.2.5 Example: a genetic circuit with internal feedback and cell-to-cell communication

The approach of the previous section will be illustrated on a chemical reaction network, taking place in a very common protein synthesis circuit in the cell of *E.Coli* in the large intestine of human beings (Pico-Marco et al. 2016).

We first make a short review about this protein synthetic pathway and expression system. In the large intestine of human beings, it is shown that heterologous protein synthesis starts by introducing an exogenous protein-coding gene in the cell, producing the corresponding protein. The ultimate goal of this circuit is to control the expression of an heterologous protein of interest which could be encoded in the same coding sequence as LuxI. Therefore, the control of LuxI will be tantamount to that of the protein of interest except for its translation step (Guimaraes et al. 2014).

The proposed gene synthetic circuit is shown in Figure 3.1 (Pico-Marco et al. 2016). For convenience, here we simplify the gene synthetic circuit which can be considered as follows: when the cell of *E.Coli* receives a 'message' from the environment (a kind of *transcription process* from extracellular space into *E.Coli* cell), three chemical reactions will take place at the intercellular level:

$$\mathrm{LuxR} + \mathrm{AHL} \rightleftharpoons \mathrm{LuxR} - \mathrm{AHL}$$

$$2(\mathrm{LuxR} - \mathrm{AHL}) \rightleftharpoons (\mathrm{LuxR} - \mathrm{AHL})_2$$

$$(\mathrm{LuxR} - \mathrm{AHL})_2 + \mathrm{DNA} \rightleftharpoons \mathrm{DNA} - (\mathrm{LuxR} - \mathrm{AHL})_2$$

When the chemical reaction network reaches an equilibrium state, the cell will send out a 'message' to the environment (a *reversed transcription process*). This is a very efficient gene circuit for adjustment of the concentrations on different kinds of protein in *E.Coli* cell, with internal feedback and cell-to-cell communication.

Let us denote the concentration of the species

$$\mathrm{LuxR}, \mathrm{AHL}, \mathrm{LuxR}-\mathrm{AHL}, (\mathrm{LuxR}-\mathrm{AHL})_2, \mathrm{DNA}, \mathrm{DNA}-(\mathrm{LuxR}-\mathrm{AHL})_2$$

by $x_1, x_2, x_3, x_4, x_5, x_6$. Hence, the state vector is defined as $z = [x_1, \ldots, x_6, U]^{tr}$ and the gradient vector of Hamiltonian function $\mathrm{H} = -S$ is given as

$$\frac{d(-S)}{dz} = [\frac{\mu_1}{T}, \ldots, \frac{\mu_6}{T}, \frac{1}{T}]^{tr}$$

With $m = 6$, $r = 3$ and $c = 5$, the stoichiometric matrix $C \in \mathbb{R}^{6\times 3}$ is written as

$$C = \begin{bmatrix} -1 & 0 & 0 \\ -1 & 0 & 0 \\ 1 & -2 & 0 \\ 0 & 1 & -1 \\ 0 & 0 & -1 \\ 0 & 0 & 1 \end{bmatrix}$$

The complex composition matrix $Z \in \mathbb{R}^{6\times 5}$ becomes

$$Z = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

while the incidence matrix $B \in \mathbb{R}^{5\times 3}$ is

$$B = \begin{bmatrix} -1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \\ 0 & 0 & 1 \end{bmatrix}$$

Since the chemical reactions take place naturally when the cell receives the 'message' from the environment, this means that the activation energies in the Arrhenius equation are so small that they can be ignored, i.e.,

$E_j^f = 0, j = 1, \ldots, r$

$E_j^b = 0, j = 1, \ldots, r$

Hence, the matrix of conductances K becomes independent of T, and takes the form

$$K = \begin{bmatrix} x_3^* & 0 & 0 \\ 0 & \frac{(x_3^*)^2}{35} & 0 \\ 0 & 0 & \frac{(x_3^*)^2 x_5^*}{4900} \end{bmatrix}$$

where $x^* = [x_1^*, x_2^*, x_3^*, x_4^*, x_5^*, x_6^*]^{tr}$ is a thermodynamic equilibrium. Therefore, the Laplacian matrix $L = BKB^{tr} \in \mathbb{R}^{5\times 5}$ is equal to

$$L = \begin{bmatrix} x_3^* & -x_3^* & 0 & 0 & 0 \\ -x_3^* & x_3^* + \frac{2x_3^{*2}}{35} & \frac{-2x_3^{*2}}{35} & 0 & 0 \\ 0 & \frac{-2x_3^{*2}}{35} & \frac{2x_3^{*2}}{35} & 0 & 0 \\ 0 & 0 & 0 & \frac{x_3^{*2}x_5^*}{4900} & \frac{-x_3^{*2}x_5^*}{4900} \\ 0 & 0 & 0 & \frac{-x_3^{*2}x_5^*}{4900} & \frac{x_3^{*2}x_5^*}{4900} \end{bmatrix}$$

which is independent of T as well. Therefore, the port-Hamiltonian formulation (3.17) for the genetic protein synthesis circuit is

$$\begin{bmatrix} x_1 \\ \vdots \\ x_6 \\ U \end{bmatrix} = (\mathcal{J} - \mathcal{R}) \begin{bmatrix} \frac{\mu_1}{T} \\ \vdots \\ \frac{\mu_6}{T} \\ -\frac{1}{T} \end{bmatrix}$$

where the matrix $(\mathcal{J} - \mathcal{R})(\frac{d(-S)}{dz})$ can be written as

$$\begin{bmatrix} \mathbf{0}_{6\times 6} & p \\ p^{tr} & r \end{bmatrix}$$

where $p = [p_1, p_2, p_3, p_4, p_5, p_6]^{tr} \in \mathbb{R}^6$ and $r \in \mathbb{R}$, with

$$
\begin{aligned}
p_1 &= -Tx_3^*(\exp(\tfrac{\mu_1+\mu_2}{RT}) - \exp\tfrac{\mu_3}{RT}) \\
p_2 &= -Tx_3^*(\exp(\tfrac{\mu_1+\mu_2}{RT}) - \exp\tfrac{\mu_3}{RT}) \\
p_3 &= Tx_3^*(\exp(\tfrac{\mu_1+\mu_2}{RT}) - \exp\tfrac{\mu_3}{RT}) - T\tfrac{x_3^{*2}}{35}(2\exp\tfrac{\mu_3}{RT} - 2\exp\tfrac{\mu_4}{RT}) \\
p_4 &= T\tfrac{x_3^{*2}}{35}(2\exp\tfrac{\mu_3}{RT} - 2\exp\tfrac{\mu_4}{RT}) - T\tfrac{x_3^{*2}x_5}{4900}(\exp(\tfrac{\mu_4+\mu_5}{RT}) - \exp\tfrac{\mu_6}{RT}) \\
p_5 &= -T\tfrac{x_3^{*2}x_5}{4900}(\exp(\tfrac{\mu_4+\mu_5}{RT}) - \exp\tfrac{\mu_6}{RT}) \\
p_6 &= -T\tfrac{x_3^{*2}x_5}{4900}(\exp(\tfrac{\mu_4+\mu_5}{RT}) - \exp\tfrac{\mu_6}{RT}) \\
r &= (\mu_1+\mu_2)[Tx_3^*(\exp(\tfrac{\mu_1+\mu_2}{RT}) - \exp\tfrac{\mu_3}{RT}] + \mu_3[-Tx_3^*(\exp(\tfrac{\mu_1+\mu_2}{RT}) - \exp\tfrac{\mu_3}{RT}) \\
&\quad + T\tfrac{x_3^{*2}}{35}(2\exp\tfrac{\mu_3}{RT} - 2\exp\tfrac{\mu_4}{RT})] + \mu_4[-T\tfrac{x_3^{*2}}{35}(2\exp\tfrac{\mu_3}{RT} - 2\exp\tfrac{\mu_4}{RT}) \\
&\quad + T\tfrac{x_3^{*2}x_5}{4900}(\exp(\tfrac{\mu_4+\mu_5}{RT}) - \exp\tfrac{\mu_6}{RT})] + (\mu_5+\mu_6)[T\tfrac{x_3^{*2}x_5}{4900}(\exp(\tfrac{\mu_4+\mu_5}{RT}) - \exp\tfrac{\mu_6}{RT})]
\end{aligned}
$$

3.3 Thermodynamic equilibria and asymptotic stability

The discussion in Sect. 3.2 is based on the assumption of existence of a thermodynamic equilibrium. Starting from the definition of a thermodynamic equilibrium of non-isothermal chemical reaction networks, we will derive in this section a full characterization of the set of equilibria, analogous to the case of isothermal chemical reaction networks in (van der Schaft et al. 2013a).

Subsequently, for stability analysis, we will use as Lyapunov function the availability function which is directly based on the quasi port-Hamiltonian representation given in (3.15), (3.16) and (3.17). Note that the use of availability functions for stability analysis is classical, see e.g. (Keenan 1951), (Hoang, Couenne, Jallut and Gorrec 2011), (Hoang, Couenne, Jallut and Gorrec 2012).

3.3.1 Thermodynamic equilibria

In this section, the existence of a thermodynamic equilibrium will be derived in the following linear-algebraic way (Feinberg 1989). Recall the definition of a thermodynamic equilibrium for non-isothermal chemical reaction networks from Sect. 3.2. Let z^* be a thermodynamic equilibrium under a certain temperature T, i.e., $v(z^*) = 0$.

This implies that for any $j = 1, \ldots, r$,

$$k_j^f \exp(-\frac{E_j^f}{RT}) \exp(Z_{\mathcal{S}_j}^{tr} \mathrm{Ln}(x^*)) - k_j^b \exp(-\frac{E_j^b}{RT}) \exp(Z_{\mathcal{P}_j}^{tr} \mathrm{Ln}(x^*)) = 0$$

or equivalently

$$k_j^f \exp(-\frac{E_j^f}{RT}) \exp(Z_{\mathcal{S}_j}^{tr} \mathrm{Ln}(x^*)) = k_j^b \exp(-\frac{E_j^b}{RT}) \exp(Z_{\mathcal{P}_j}^{tr} \mathrm{Ln}(x^*))$$

These equations are referred to as the detailed balance equations. Denote

$$K_j^{eq}(T) := \frac{k_j^f}{k_j^b} \exp(\frac{E_j^b - E_j^f}{RT}) = \exp(Z_{\mathcal{P}_j}^{tr} \mathrm{Ln}(x^*) - Z_{\mathcal{S}_j}^{tr} \mathrm{Ln}(x^*))$$

Collecting all chemical reactions from 1 to r, and making use of the incidence matrix B, we obtain the following condition for a thermodynamical equilibrium $x^*(T)$

$$K^{eq}(T) = \mathrm{Exp}\,(B^{tr} Z^{tr} \mathrm{Ln}(x^*(T))) = \mathrm{Exp}\,(C^{tr} \mathrm{Ln}(x^*(T))) \tag{3.22}$$

where $K^{eq}(T)$ is the r-dimensional vector with jth element $K_j^{eq}(T)$, which is dependent on the temperature T. Therefore, for a given temperature T, there exists a thermodynamic equilibrium $x^*(T) \in \mathbb{R}_+^m$ if and only if $k_j^f > 0$, $k_j^b > 0$ for all $j = 1, \ldots, r$, and

$$\mathrm{Ln}\,(K^{eq}(T)) \in \mathrm{im}\, C^{tr}$$

In general, the equilibrium concentration $x^*(T)$ may not be unique. Let $x^{**}(T)$ be another thermodynamic equilibrium for the same temperature T. Then

$$K^{eq}(T) = \mathrm{Exp}\,(C^{tr} \mathrm{Ln}(x^{**})) = \mathrm{Exp}\,(C^{tr} \mathrm{Ln}(x^*)) \tag{3.23}$$

That is to say, for a certain temperature T, once one thermodynamic equilibrium $x^*(T)$ is given, the whole set of thermodynamic equilibria at the same temperature T can be found. Furthermore, since $dU = 0$, we have $U^* = U^{**}$. Denote $z^* = (x^*(T), U^*)$ and $z^{**}(T) = (x^{**}(T), U^{**})$, then it follows that the set of thermodynamic equilibria for the same temperature T can be written as

$$\Sigma_T = \left\{ z^{**} = (x^{**}(T), U^{**}) \mid C^{tr} \mathrm{Ln}(x^{**}(T)) = C^{tr} \mathrm{Ln}(x^*(T)), U^* = U^{**} \right\} \tag{3.24}$$

This directly extends the classical result for isothermal chemical reaction networks, see e.g. (van der Schaft et al. 2013a). Note that the value of the terms $\mathrm{Exp}(C^{tr}\mathrm{Ln}(x^*))$ depends on the temperature T, while the relation $\mathrm{Exp}(C^{tr}\mathrm{Ln}(x^{**})) = \mathrm{Exp}(C^{tr}\mathrm{Ln}(x^*))$ is not dependent on the temperature T.

Since $K^{eq}(T) = \mathrm{Exp}\,(C^{tr}\mathrm{Ln}(x^*))$ as a function of T is monotone and injective, it follows that the set of thermodynamic equilibria Σ_{T_1} is disjoint from Σ_{T_2} whenever $T_1 \neq T_2$. I.e., $\Sigma_{T_1} \cap \Sigma_{T_2} = \varnothing$ for any $T_1 \neq T_2$.

3.3.2 Asymptotic stability

For isothermal chemical reaction networks, it was shown in (Horn and Jackson 1972), (van der Schaft et al. 2013a) and (van der Schaft et al. 2013b), that the Gibbs' free energy can be used as a Lyapunov function for proving asymptotic stability towards a unique equilibrium depending on the initial condition. In this section we aim at proving a similar result for the non-isothermal case based on the port-Hamiltonian formulation obtained in the previous section, employing the availability function. Note that this is different from what has been done in Sect. 2.4.2 (as well in (Ramırez, Le Gorrec, Maschke and Couenne 2013) and (Wang et al. 2016)), where an energy-based availability function was employed.

We define the entropy-based availability function as

$$A(z) := -S(z) + S(z^o) + \frac{\partial^{tr} S}{\partial z}(z^o)(z - z^o) \tag{3.25}$$

where z^o is a reference point taken as a thermodynamic equilibrium, cf. Sect. 3.2.

Theorem 3.2. *Consider a detailed balanced chemical reaction network given by (3.15), (3.16) and (3.17), with z^o a thermodynamic equilibrium. Define $A(z) : \mathbb{R}_+^{m+1} \to \mathbb{R}$ given by (3.25). Then A has a strict minimum at z^o with $A(z^o) = 0$, while the time-derivative of $A(z)$, $\frac{dA}{dt}$ is less than or equal to zero with equality only at z^o.*

Proof. It has been proved that for homogeneous mixtures, the entropy function is necessarily concave (Callen 1960). Moreover, the entropy is strictly concave if at least one global extensive property (such as volume, total mass, or total mole number) is fixed, see (Alonso and Ydstie 2001) and (Jillson and Ydstie 2007). Recall the assumption that the chemical reaction network is isochoric, i.e. $dV = 0$, so the entropy is strictly concave and $A(z)$ has a strict minimum at z^o. Moreover, the time

derivative of $A(z)$ is given as

$$\begin{aligned}
\tfrac{dA}{dt} &= \tfrac{\partial A}{\partial z}(z)\dot{z} \\
&= -(\tfrac{dS}{dz}(z) - \tfrac{dS}{dz}(z^o))^{tr}\tfrac{dz}{dt} \\
&= -[\tfrac{(\mu^o)^{tr}}{T^o} - \tfrac{(\mu)^{tr}}{T}, \tfrac{1}{T} - \tfrac{1}{T^o}] \\
&\qquad \times \begin{bmatrix} \mathbf{0}_{m\times m} & TZL\mathrm{Exp}(\tfrac{Z^{tr}\mu}{RT}) \\ -T(ZL\mathrm{Exp}(\tfrac{Z^{tr}\mu}{RT}))^{tr} & -T\mu^{tr}ZL\mathrm{Exp}(\tfrac{Z^{tr}\mu}{RT}) \end{bmatrix} \begin{bmatrix} \frac{\mu}{T} \\ -\frac{1}{T} \end{bmatrix} \\
&= -(\tfrac{\mu^{tr}Z}{T} - \tfrac{(\mu^o)^{tr}Z}{T^o})L\mathrm{Exp}(\tfrac{Z^{tr}\mu}{RT}) \\
&= -R\gamma^{tr}L\mathrm{Exp}(\gamma) + R(\gamma^o)^{tr}L\mathrm{Exp}(\gamma)
\end{aligned} \tag{3.26}$$

where $\mu = RT\mathrm{Ln}\frac{x}{x^*}$ is the vector of chemical potentials, $\mu^o = RT^o\mathrm{Ln}\frac{x^o}{x^*}$, $\gamma = \frac{Z^{tr}\mu}{RT} = Z^{tr}\mathrm{Ln}\frac{x}{x^*}$ and $\gamma^o = \frac{Z^{tr}\mu^o}{RT^o} = Z^{tr}\mathrm{Ln}\frac{x^o}{x^*}$. Since x^* and x^o are both thermodynamic equilibria, we obtain from equation (3.23)

$$C^{tr}\mathrm{Ln}(x^o) = C^{tr}\mathrm{Ln}(x^*),$$

which is equal to

$$C^{tr}\mathrm{Ln}(\frac{x^o}{x^*}) = (ZB)^{tr}\mathrm{Ln}(\frac{x^o}{x^*}) = \mathbf{0}_c$$

Therefore, we have

$$B^{tr}(Z^{tr}\mathrm{Ln}(\frac{x^o}{x^*})) = B^{tr}\gamma^o = \mathbf{0}_c$$

Recall that since L is a balanced weighted Laplacian matrix, for any $\gamma \in \mathbb{R}^c$, we have $\gamma^{tr}L\mathrm{Exp}(\gamma) \geqslant 0$, while $\gamma^{tr}L\mathrm{Exp}(\gamma) = 0$ if and only if $B^{tr}\gamma = 0$ (van der Schaft et al. 2013a). Hence

$$(\gamma^o)^{tr}L\mathrm{Exp}(\gamma^o) = 0$$

Therefore the time derivative of $A(z)$ satisfies

$$\frac{dA}{dt} = -R\gamma^{tr}L\mathrm{Exp}(\gamma) \leqslant 0$$

□

Let the system converge to a point denoted as

$$z^* \in \Sigma_{T^*}$$

and denote the equilibrium temperature associated with the equilibrium point z^* by T^*. We know that at equilibrium, the entropy is maximal, implying that

$$\frac{dS}{dt}|_{z=z^*} = 0$$

This is a classical statement in chemical engineering, and is comparable with the statement in (Rao and Esposito 2016), where for isothermal systems the Gibbs' free energy is minimized. According to equation (3.20), we have

$$\sigma|_{z=z^*} = 0 \tag{3.27}$$

and for an isolated system we have

$$dU = 0 \tag{3.28}$$

By using the equations (3.27) and (3.28), the equilibrium point z^* and T^* can be determined. Then, by using a similar argument as in (Feinberg 1995) and (van der Schaft et al. 2013a) , the following theorem will imply the asymptotic stability towards the set Σ_{T^*}.

Theorem 3.3. *Consider the detailed balanced chemical reaction network given by (3.15), (3.16) and (3.17) with $T \in \mathbb{R}_+$. Then for any $x_1 \in \mathbb{R}^m_+$, $T_1 \in \mathbb{R}_+$, there exists a unique $x^* \in \mathbb{R}^m_+$ and $T^* \in \mathbb{R}_+$, such that $x^* - x_1 \in \operatorname{im} C$, and $z^* = (x^*, U^*(x^*, T^*)) \in \Sigma_{T^*}$, $z^* \in \mathbb{R}^{m+1}_+$.*

Proof. Let $W = \operatorname{im} C$. Then $W^\perp = \ker C^{tr}$. Let $z_1(x_1, T_1) \in \mathbb{R}^{m+1}_+, z^{**}(x^{**}, T^*) \in \mathbb{R}^{m+1}_+$, where $z^{**}(x^{**}, T^*) \in \Sigma_{T^*}$ is a thermodynamic equilibrium for temperature T^*. As proved in (Feinberg 1995), (van der Schaft et al. 2013a), there exists a unique $\beta \in \ker C^{tr}$ such that $x^{**}\mathrm{Exp}(\beta) - x_1 \in \operatorname{im} C$. Define $z^*(x^*, T^*) \in \mathbb{R}^{m+1}_+$ with $x^* = x^{**}\mathrm{Exp}(\beta)$. Clearly, $C^{tr}\beta = C^{tr}\mathrm{Ln}(\frac{x^*}{x^{**}}) = 0$, which is in line with (3.23) so that $z^*(x^*, T^*) \in \Sigma_{T^*}$. Moreover, we have $x^* - x_1 = x^{**}\mathrm{Exp}\beta - x_1 \in \operatorname{im} C$.

Combining with Theorem 3.1, this implies that the equilibrium z^* is asymptotically stable with respect to all initial conditions near z^*. Hence the asymptotic stability of the quasi port-Hamiltonian system defined by (3.15), (3.16) and (3.17) is proved. □

3.3.3 Example: a genetic circuit with internal feedback and cell-to-cell communication (continued)

Recall the genetic protein synthesis circuit described in Sect. 3.2.5. At thermodynamic equilibrium z^*, we have $v(z^*) = 0$. It can be verified that the equilibrium set Σ_T is the 3-dimensional set given as

$$\Sigma_T = \left\{ \begin{array}{l} (x_1^*, \ldots, x_6^*, T^*)^{tr} \mid x_1^* = \frac{150 x_3^*}{x_2^*}, x_4^* = \frac{(x_3^*)^2}{35}, x_6^* = \frac{(x_3^*)^2 x_5^*}{4900}, \\ x_i^* \in \mathbb{R}_+^m, i = 1 \ldots 6, T^* \in \mathbb{R}_+^m \end{array} \right\}$$

To study its asymptotic stability, we define the availability function as in (3.25), i.e.,

$$A(z) = -S(z) + S(z) + \frac{\partial^{tr} S}{\partial z}(z^o)(z - z^o) \tag{3.29}$$

where the reference point z^o is taken to be a thermodynamic equilibrium for the temperature T. We have $A(z) = 0$ at $z = z^o$, and as discussed in Sect. 2.4, the time derivative of $A(z)$ can be written as

$$\begin{aligned} \tfrac{dA}{dt} &= -(\tfrac{dS}{dz} - \tfrac{dS}{dz}(z^o))^{tr} \tfrac{dz}{dt} \\ &= -R\gamma^{tr} L\mathrm{Exp}(\gamma) + R\gamma^{otr} L\mathrm{Exp}(\gamma) \\ &= -R\gamma^{tr} L\mathrm{Exp}(\gamma) \leqslant 0 \end{aligned} \tag{3.30}$$

Therefore $A(z)$ is a well-defined Lyapunov function. The port-Hamiltonian system (3.17) for the genetic protein synthesis circuit is asymptotically stable under temperature T.

3.4 Chemical reaction networks with ports

In many application areas, the chemical reaction networks under consideration are not isolated. That is to say, there exists mass exchange or heat exchange between the chemical reaction network and its environment.

In this section we will extend the port-Hamiltonian formulation for non-isothermal chemical reaction networks to the case of mass and heat exchange. As in the previous work, see (Hoang, Couenne, Jallut and Gorrec 2011), (Hoang, Couenne, Jallut and Gorrec 2012), (Ramırez, Le Gorrec, Maschke and Couenne 2013) and

(Ramirez et al. 2014), when modeling and control of the Continuous Stirred Tank Reactor (CSTR), we define 'external ports' as the inflow/outflow of a mixture. Furthermore, we suppose that the output flow is such that the volume and pressure are constant (Couenne et al. 2006).

Then equation (2.2) can be rewritten as

$$\dot{x} = Cv + F_{in} - F_{out} \tag{3.31}$$

where the vectors F_{in} and F_{out} are respectively the input and output concentration flows. Then the previous formulation (3.17) can be extended to non-isothermal chemical reaction network with external ports as

$$\dot{z} \quad = (\mathcal{J}(\tfrac{\partial \mathrm{H}}{\partial z}) - \mathcal{R}(\tfrac{\partial \mathrm{H}}{\partial z}))\tfrac{\partial \mathrm{H}}{\partial z}(z) + \begin{bmatrix} F_{in} - F_{out} \\ \Delta U \end{bmatrix} \tag{3.32}$$

where as before the Hamiltonian function is given as $\mathrm{H} = -S$ with S the entropy of system. The internal energy U is written as

$$U = \sum_{i=1}^{m} x_i(c_{pi}(T - T_0) - u_{0i})$$

where c_{pi}, u_{0i} T_0 are respectively the heat capacity at constant pressure, reference molar energy and reference temperature. With constant volume and pressure the balance equation for the internal energy U is written as

$$\Delta U = Q + \sum_{i=1}^{m}(F_{in}^i h_{in}^i - F_{out}^i h_{out}^i)$$

where Q is the heat flux from the environment, and F_{in}^i and F_{out}^i are the ith element of F_{in} and F_{out}. Furthermore, h_{in}^i and h_{out}^i are respectively the input and output specific enthalpies.

Note that in the port-Hamiltonian formulation for non-isothermal chemical reaction network with ports (3.32), we still use the thermodynamic equilibrium $z^*(T)$ for the chemical reaction network without ports under given temperature T, as defined in Sect. 3.2.

As before, in order to verify asymptotic stability, we define the availability equation as

$$A(z) = -S(z) + S(z^o) + \frac{\partial^{tr} S}{\partial z}(z^o)(z - z^o) \tag{3.33}$$

It then remains to prove that $A(z)$ is a Lyapunov function. Obviously, we have $A(z^o) = 0$.

The main assumption we will make is that $\Delta F = F_{in} - F_{out}$ is a vector which can be described by mass action kinetics. That is to say, it can be expanded as

$$\Delta F = -ZL'\mathrm{Exp}(Z^{tr}\mathrm{Ln}\frac{x}{x^*}) = -ZL'\mathrm{Exp}(\frac{Z^{tr}\mu}{RT})$$

with $L' = B'K'(B')^{tr}$ a constant balanced weighted Laplacian matrix corresponding to another incidence matrix $B' \in \mathbb{R}^{c\times r'}$ with $r' \in \mathbb{N}$, and another matrix of conductance $K' \in \mathbb{R}^{r'\times r'}$, and $\Delta U = 0$. Note that under this assumption, the external ports added to the network can be considered as another chemical reaction network, with m species, r' chemical reactions and c chemical complexes. Therefore, it can be represented with the same complex composition matrix Z, but with a different incidence matrix B' and a different matrix of conductance K'.

Then the time derivative of $A(z)$ becomes

$$\begin{aligned}
\tfrac{dA}{dt} &= -(\tfrac{dS}{dz} - \tfrac{dS}{dz}(z^o))^{tr}\tfrac{dz}{dt} \\
&= -\begin{bmatrix} \frac{\mu^o}{T^o} - \frac{\mu}{T} & \frac{1}{T} - \frac{1}{T^o} \end{bmatrix}^{tr} \\
&\qquad \left(\begin{bmatrix} \mathbf{0}_{m\times m} & TZL\mathrm{Exp}(\frac{Z^{tr}\mu}{RT}) \\ -T(ZL\mathrm{Exp}(\frac{Z^{tr}\mu}{RT}))^{tr} & -T\mu^{tr}ZL\mathrm{Exp}(\frac{Z^{tr}\mu}{RT}) \end{bmatrix} + \begin{bmatrix} \Delta F \\ \Delta U \end{bmatrix}\right) \\
&= -(\tfrac{\mu}{T} - \tfrac{\mu^o}{T^o})^{tr}ZL\mathrm{Exp}(\tfrac{Z^{tr}\mu}{RT}) + (\tfrac{\mu}{T} - \tfrac{\mu^o}{T^o})^{tr}\Delta F - (\tfrac{1}{T} - \tfrac{1}{T^o})\Delta U \\
&= -R(\gamma - \gamma^o)^{tr}L\mathrm{Exp}(\gamma) - R(\gamma - \gamma^o)^{tr}L'\mathrm{Exp}(\gamma) \\
&= -R\gamma^{tr}L\mathrm{Exp}(\gamma) - R\gamma^{tr}L'\mathrm{Exp}(\gamma)
\end{aligned}$$

Since

$$-R\gamma^{tr}L\mathrm{Exp}(\gamma) \leqslant 0$$

$$-R\gamma^{tr}L'\mathrm{Exp}(\gamma) \leqslant 0$$

we have $\frac{dA}{dt} \leqslant 0$, and thus the port-Hamiltonian system for non-isothermal chemical reaction networks with ports is asymptotically stable for temperature T. Let us illustrate this on the following example.

3.4.1 Example: a genetic circuit with internal feedback and cell-to-cell communication (continued)

Recall the genetic protein synthesis circuit described in Sect. 3.2.5. Assume that there exists a port of flows $\Delta F = -ZL'\mathrm{Exp}(Z^{tr}\mathrm{Ln}\frac{x}{x^*})$ with

$$L' = B\begin{bmatrix} l_1 & 0 & 0 \\ 0 & l_2 & 0 \\ 0 & 0 & l_3 \end{bmatrix}B^{tr} = \begin{bmatrix} l_1 & -l_1 & 0 & 0 & 0 \\ -l_1 & l_1+2l_2 & -2l_2 & 0 & 0 \\ 0 & -2l_2 & 2l_2 & 0 & 0 \\ 0 & 0 & 0 & l_3 & -l_3 \\ 0 & 0 & 0 & -l_3 & l_3 \end{bmatrix}$$

where l_1, l_2 and l_3 are positive constants. Then the port-Hamiltonian formulation (3.17) extends to

$$\begin{bmatrix} x_1 \\ \vdots \\ x_6 \\ U \end{bmatrix} = (\mathcal{J}-\mathcal{R})\begin{bmatrix} \frac{\mu_1}{T} \\ \vdots \\ \frac{\mu_6}{T} \\ -\frac{1}{T} \end{bmatrix} + \begin{bmatrix} F_{in}-F_{out} \\ \\ \Delta U \end{bmatrix}$$

where the matrix $\mathcal{J}-\mathcal{R}$ is equal to

$$\begin{bmatrix} \mathbf{0}_{6\times 6} & p \\ p^{tr} & r \end{bmatrix}$$

where $p = [p_1, p_2, p_3, p_4, p_5, p_6]^{tr}$ and $r \in \mathbb{R}$, with

$$\begin{aligned}
p_1 &= -Tx_3^*(\exp(\tfrac{\mu_1+\mu_2}{RT}) - \exp\tfrac{\mu_3}{RT}) \\
p_2 &= -Tx_3^*(\exp(\tfrac{\mu_1+\mu_2}{RT}) - \exp\tfrac{\mu_3}{RT}) \\
p_3 &= Tx_3^*(\exp(\tfrac{\mu_1+\mu_2}{RT}) - \exp\tfrac{\mu_3}{RT}) - T\tfrac{x_3^{*2}}{35}(2\exp\tfrac{\mu_3}{RT} - 2\exp\tfrac{\mu_4}{RT}) \\
p_4 &= T\tfrac{x_3^{*2}}{35}(2\exp\tfrac{\mu_3}{RT} - 2\exp\tfrac{\mu_4}{RT}) - T\tfrac{x_3^{*2}x_5}{4900}(\exp(\tfrac{\mu_4+\mu_5}{RT}) - \exp\tfrac{\mu_6}{RT}) \\
p_5 &= -T\tfrac{x_3^{*2}x_5}{4900}(\exp(\tfrac{\mu_4+\mu_5}{RT}) - \exp\tfrac{\mu_6}{RT}) \\
p_6 &= -T\tfrac{x_3^{*2}x_5}{4900}(\exp(\tfrac{\mu_4+\mu_5}{RT}) - \exp\tfrac{\mu_6}{RT}) \\
r &= (\mu_1+\mu_2)[Tx_3^*(\exp(\tfrac{\mu_1+\mu_2}{RT}) - \exp\tfrac{\mu_3}{RT}] + \mu_3[-Tx_3^*(\exp(\tfrac{\mu_1+\mu_2}{RT}) - \exp\tfrac{\mu_3}{RT}) \\
&\quad +T\tfrac{x_3^{*2}}{35}(2\exp\tfrac{\mu_3}{RT} - 2\exp\tfrac{\mu_4}{RT})] + (\mu_5+\mu_6)[T\tfrac{x_3^{*2}x_5}{4900}(\exp(\tfrac{\mu_4+\mu_5}{RT}) - \exp\tfrac{\mu_6}{RT})] \\
&\quad +T\tfrac{x_3^{*2}x_5}{4900}(\exp(\tfrac{\mu_4+\mu_5}{RT}) - \exp\tfrac{\mu_6}{RT})] + \mu_4[-T\tfrac{x_3^{*2}}{35}(2\exp\tfrac{\mu_3}{RT} - 2\exp\tfrac{\mu_4}{RT})
\end{aligned}$$

and with

$$\begin{bmatrix} F_{in} - F_{out} \\ \Delta U \end{bmatrix} = \begin{bmatrix} \Delta F \\ 0 \end{bmatrix} = \begin{bmatrix} -ZL'\mathrm{Exp}(Z^{tr}\mathrm{Ln}\frac{x}{x^*}) \\ 0 \end{bmatrix}$$

Then the availability function (3.33) can be rewritten as

$$A(z) = -S(z) + S(z^o) + \frac{\partial^{tr} S}{\partial z}(z^o)(z - z^o) \tag{3.34}$$

$A(z^o) = 0$ and the time derivative of $A(z)$ becomes

$$\begin{aligned} \frac{dA}{dt} &= -(\frac{dS}{dz} - \frac{dS}{dz}(z^o))^{tr}\frac{dz}{dt} \\ &= -R\gamma^{tr}L\mathrm{Exp}(\gamma) - \gamma^{tr}L'\mathrm{Exp}(\gamma) \leqslant 0 \end{aligned}$$

Hence $A(z)$ is a well-defined Lyapunov function. We conclude that the port-Hamiltonian system for genetic protein synthesis circuit with a specific port ΔF is asymptotically stable for temperature T.

3.5 Conclusion

In this chapter, a quasi port-Hamiltonian formulation has been developed for non-isothermal mass action kinetics chemical reaction networks. Expanding the port-Hamiltonian formulation of isothermal chemical reaction networks, and based on the mass balance and energy balance equations, this port-Hamiltonian formulation provides us with an explicit way to represent the chemical reaction networks and their thermodynamic properties, including the entropy balance and the conditions for the existence of thermodynamic equilibrium. Moreover, this quasi port-Hamiltonian formulation and its thermodynamic analysis have been extended to non-isothermal chemical reaction networks with external ports. The results have been illustrated on a chemical reaction network in our body: the genetic circuit with internal feedback and cell-to-cell communication.

The irreversible port-Hamiltonian formulation given by (2.21) in the previous chapter, and the quasi port-Hamiltonian formulation given by (3.17) provide us two way to model non-isothermal chemical reaction networks. We can make use of either of them depending on the physical structure of system.

Chapter 4

Port-Hamiltonian structure for interconnected chemical reaction networks

4.1 Introduction

In this chapter, we are interested in the interconnection of two chemical reaction networks governed by mass action kinetics, which separately can be modeled by the quasi port-Hamiltonian formulation in (3.17). Interconnection of chemical reaction networks is an interesting subject in chemical and biological domains discussed in some previous work, see for example (Papachristodoulou and Recht 2007) and (Prior and Rosseinsky 2003). This chapter is inspired by (van der Schaft et al. 2013a) where the port-Hamiltonian modeling for interconnected chemical reaction networks have been introduced. The most basic way to connect the chemical reaction networks is through shared boundary chemical species. In this dissertation, in order to develop a port-Hamiltonian structure for the interconnected chemical reaction networks, we offer two ways to deal with interconnection by shared species, one in Sect. 4.2 and another in Sect. 4.3.

In Sect. 4.2, the two chemical reaction networks interconnect to each other by considering that the two reactors get together and thus the shared species can be considered directly as the same species, see Figure 4.1. In Sect. 4.3, the interconnection arises from *power-port interconnection* at the shared chemical species. There is a sort of transformation of mass and energy between the shared species in each reactor, see Figure 4.3.

4.2 Interconnection arising from boundary species

In this section, the interconnection can be considered as an interaction of a chemical reaction network with another chemical reaction network by putting the two chemical reaction networks together and identifying the shared species in each reactor as the same species.

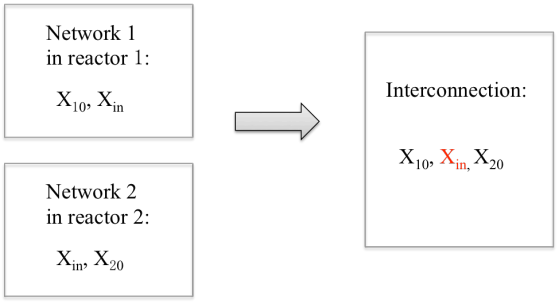

Figure 4.1: Interconnection through shared boundary species.

The main idea of interconnection is as follows, see Figure 4.1. Assume that there are two closed chemical reaction networks, which means they have no mass or energy exchange with the environment. In each chemical reaction network, the species can be divided into two groups. One group of species consists of the species that appear only in one of the chemical reaction networks, called the non-shared species, denoted as X_{10} for the network 1 and X_{20} for the network 2. Another group of species is the species that appear in both of the two chemical reaction networks, called the shared chemical species, denoted as X_{in}. Once the two chemical reaction networks interconnect to each other, the species in the whole chemical reaction network are denoted by X_{10}, X_{in} and X_{20}. Note that there may exist complexes, referred to as *shared complexes*, which only consist of shared species.

In order to simplify the interconnection, we suppose that the reactions in each chemical network proceed slowly compared to the diffusion in each reactor and the heat transfer between the two chemical reaction networks. That means, the temperature T and pressure P can be considered to vary synchronously in each reactor and we have $T = T_1 = T_2$ and $P = P_1 = P_2$.

4.2.1 Notations

Consider two non-isothermal chemical reaction networks which can be modeled by the port-Hamiltonian formulation (3.17). One is composed of r_1 reactions, m_1 species and c_1 complexes, while the other consists of r_2 reactions, m_2 species and c_2 complexes. In each chemical network, the species can be divided into two groups, the non-shared and the shared species, i.e., $m_1 = m_{10} + m_{\text{in}}$ and $m_2 = m_{20} + m_{\text{in}}$. If there exist shared complexes, then we denote them as c_{in} and thus we have $c_1 = c_{10} + c_{\text{in}}$ and $c_2 = c_{20} + c_{\text{in}}$.

To simplify the notations, define $m = m_{10} + m_{\text{in}} + m_{20}$, $c = c_{10} + c_{\text{in}} + c_{20}$ and

$r = r_1 + r_2$. Let $x_{i0} \in \mathbb{R}_+^{m_{i0}}$ denote the vector of the non-shared part of concentrations in the chemical network 1 and 2, and $x_{\text{in}} \in \mathbb{R}_+^{m_{\text{in}}}$ the vector of the shared part of the concentrations of the two chemical networks. Then the vector of concentrations of interconnected networks can be written as $\hat{x} = [x_{10}, x_{\text{in}}, x_{20}]^{tr} \in \mathbb{R}_+^m$. Similarly, let $\mu_{i0} \in \mathbb{R}_+^{m_{i0}}$ denote the vector of the non-shared part of the chemical potentials of each network and $\mu_{\text{in}} \in \mathbb{R}_+^{m_{\text{in}}}$ the vector of the shared chemical potentials of the two chemical networks. Then we denote the chemical potentials of the interconnection of the two chemical networks as $\hat{\mu} = [\mu_{10}, \mu_{\text{in}}, \mu_{20}]^{tr} \in \mathbb{R}_+^m$.

Let the incidence matrix of each chemical networks 1 and 2 be denoted as B_1 and B_2. Then we have $B_1 = \begin{bmatrix} B_{10} \\ B_{\text{in}}^1 \end{bmatrix}$, $B_2 = \begin{bmatrix} B_{\text{in}}^2 \\ B_{20} \end{bmatrix}$, where $B_{i0} \in \mathbb{R}^{c_{i0} \times r_i}$ denotes the non-shared part of the incidence matrix in each chemical reaction network, and $B_{\text{in}}^i \in \mathbb{R}^{c_{\text{in}} \times r_i}$ denotes the shared part of the incidence matrix in each chemical reaction network, $i = 1, 2$. Therefore, the incidence matrix of the interconnected chemical reaction network $B \in \mathbb{R}^{c \times r}$ is given as

$$B = \begin{bmatrix} B_{10} & 0 \\ B_{\text{in}}^1 & B_{\text{in}}^2 \\ 0 & B_{20} \end{bmatrix}$$

The complex composition matrix of network 1 and 2 can be rewritten as

$$Z_1 = \begin{bmatrix} Z_{10} & 0 \\ Z'_{10} & Z_{\text{in}} \end{bmatrix}$$

$$Z_2 = \begin{bmatrix} Z_{\text{in}} & Z'_{20} \\ 0 & Z_{20} \end{bmatrix}$$

where $Z_{i0} \in \mathbb{R}^{m_{i0} \times c_{i0}}$ denotes the totally non-shared part of the complex composition matrix in each chemical reaction network, $Z'_{i0} \in \mathbb{R}^{m_{\text{in}} \times c_{i0}}$ denotes the shared species in the non-shared complexes, and $Z_{\text{in}} \in \mathbb{R}^{m_{\text{in}} \times c_{\text{in}}}$ the shared part of the complex composition matrix of the chemical network, $i = 1, 2$. Then the complex composition matrix of the interconnected chemical networks $Z \in \mathbb{R}^{m \times c}$ is given as

$$Z = \begin{bmatrix} Z_{10} & 0 & 0 \\ Z'_{10} & Z_{\text{in}} & Z'_{20} \\ 0 & 0 & Z_{20} \end{bmatrix}$$

Let C_i denote the stoichiometric matrix of chemical network 1 and 2. Thus

$$C_1 = Z_1 B_1 = \begin{bmatrix} Z_{10} B_{10} \\ Z'_{10} B_{10} + Z_{\text{in}} B^1_{\text{in}} \end{bmatrix}$$

$$C_2 = Z_2 B_2 = \begin{bmatrix} Z'_{20} B_{20} + Z_{\text{in}} B^2_{\text{in}} \\ Z_{20} B_{20} \end{bmatrix}$$

Since $C = ZB$, the stoichiometric matrix of the interconnected chemical network $C \in \mathbb{R}^{m \times r}$ can be written as

$$\begin{aligned} C &= \begin{bmatrix} Z_{10} & 0 & 0 \\ Z'_{10} & Z_{\text{in}} & Z'_{20} \\ 0 & 0 & Z_{20} \end{bmatrix} \begin{bmatrix} B_{10} & 0 \\ B^1_{\text{in}} & B^2_{\text{in}} \\ 0 & B_{20} \end{bmatrix} \\ &= \begin{bmatrix} Z_{10} B_{10} & 0 \\ Z'_{10} B_{10} + Z_{\text{in}} B^1_{\text{in}} & Z'_{20} B_{20} + Z_{\text{in}} B^2_{\text{in}} \\ 0 & Z_{20} B_{20} \end{bmatrix} \end{aligned}$$

Clearly, the stoichiometric matrix of the interconnection of the two chemical networks C is a direct combination of C_1 and C_2.

Remark 4.1. If there exist no shared complex in the interconnected chemical reaction network, then the incidence matrix takes the form

$$B = \begin{bmatrix} B_{10} & 0 \\ 0 & B_{20} \end{bmatrix} \tag{4.1}$$

and the complex composition matrix takes the form

$$Z = \begin{bmatrix} Z_{10} & 0 \\ Z'_{10} & Z'_{20} \\ 0 & Z_{20} \end{bmatrix} \tag{4.2}$$

while the stoichiometric matrix takes the form

$$C = ZB = \begin{bmatrix} Z_{10} B_{10} & 0 \\ Z'_{10} B_{10} & Z'_{20} B_{20} \\ 0 & Z_{20} B_{20} \end{bmatrix} \tag{4.3}$$

The $r \times r$ matrix of conductances $K(T)$ of the interconnected network is the direct union of the matrix of conductances of chemical networks 1 and 2, i.e.,

$$K(T) = \begin{bmatrix} K_1(T) & 0 \\ 0 & K_2(T) \end{bmatrix}$$

with corresponding weighted Laplacian matrix $L = BK(T)B^{tr}$.

4.2.2 Port-Hamiltonian structure

Now the port-Hamiltonian formulation for the interconnected network is ready to be developed. Here we will use the same state vector and Hamiltonian function as in Chapter 3. We define the state vector as $w = [\hat{x}^{tr}, U]^{tr} = [x_{10}, x_{\text{in}}, x_{20}, U]^{tr}$, where $\hat{x}$ is the vector of concentrations of the interconnected chemical reaction network, and $U = U_1 + U_2$ is the total internal energy, where U_i is the internal energy of the chemical network $i = 1, 2$. Then we define minus the entropy of the interconnected chemical reaction network $-S$ as the Hamiltonian function $\mathrm{H} = -S = -(S_1 + S_2)$, where S_i is the entropy of the chemical network $i = 1, 2$. This implies that the co-state vector corresponding to $\mathrm{H} = -S$ is

$$\frac{\partial \mathrm{H}}{\partial w} = \frac{\partial(-S)}{\partial w} = \begin{bmatrix} \frac{\mu_{10}}{T} & \frac{\mu_{\text{in}}}{T} & \frac{\mu_{20}}{T} & -\frac{1}{T} \end{bmatrix}^{tr} \tag{4.4}$$

Let $w^*(T) \in \mathbb{R}^m_+$ be a thermodynamic equilibrium for a certain temperature T. Then the dynamics of the interconnection of the two chemical reaction networks can be written as

$$\dot{\hat{x}} = -ZBK(T)B^{tr}\mathrm{Exp}(\frac{Z^{tr}\hat{\mu}}{RT}) \tag{4.5}$$

$$dU = dU_1 + dU_2 = 0 \tag{4.6}$$

It follows that the balanced interconnected network is given as

$$\dot{w} = \left(\hat{\mathcal{J}}(\frac{\partial \mathrm{H}}{\partial w}(w)) - \hat{\mathcal{R}}(\frac{\partial \mathrm{H}}{\partial w}(w))\right)\frac{\partial \mathrm{H}}{\partial w}(w) \tag{4.7}$$

where $\hat{\mathcal{J}}$ is the skew-symmetric matrix

$$\hat{\mathcal{J}}(\frac{\partial \mathrm{H}}{\partial w}(w)) := \begin{bmatrix} 0 & \cdots & 0 & M \\ \vdots & \ddots & \vdots & N \\ 0 & \cdots & 0 & O \\ -M^{tr} & -N^{tr} & -O^{tr} & 0 \end{bmatrix} \tag{4.8}$$

where the upper right block is expanded as

$$\begin{bmatrix} M \\ N \\ O \end{bmatrix} = TZL\mathrm{Exp}(\frac{Z^{tr}\hat{\mu}}{RT})$$

$$\begin{aligned}
M = \quad & T\left[Z_{10}B_{10}K_1(T)B_{10}^{tr}\mathrm{Exp}(\tfrac{Z_{10}^{tr}\mu_{10}+Z_{10}^{'tr}\mu_{\mathrm{in}}}{RT}) + Z_{10}B_{10}K_1(T)B_{\mathrm{in}}^{1tr}\mathrm{Exp}(\tfrac{Z_{\mathrm{in}}^{tr}\mu_{\mathrm{in}}}{RT})\right] \\
N = \quad & T\begin{bmatrix} (Z_{\mathrm{in}}B_{\mathrm{in}}^{1} + Z'_{10}B_{10})K_1(T)B_{10}^{tr}\mathrm{Exp}(\tfrac{Z_{10}^{'tr}\mu_{\mathrm{in}}+Z_{10}^{tr}\mu_{10}}{RT}) \\ +(Z_{\mathrm{in}}B_{\mathrm{in}}^{1} + Z'_{10}B_{10})K_1(T)B_{\mathrm{in}}^{1tr}\mathrm{Exp}(\tfrac{Z_{\mathrm{in}}^{tr}\mu_{\mathrm{in}}}{RT}) \\ +(Z_{\mathrm{in}}B_{\mathrm{in}}^{2} + Z'_{20}B_{20})K_2(T)B_{\mathrm{in}}^{2tr}\mathrm{Exp}(\tfrac{Z_{\mathrm{in}}^{tr}\mu_{\mathrm{in}}}{RT}) \\ +(Z_{\mathrm{in}}B_{\mathrm{in}}^{2} + Z'_{20}B_{20})K_2(T)B_{20}^{tr}\mathrm{Exp}(\tfrac{Z_{20}^{tr}\mu_{20}+Z_{20}^{'tr}\mu_{\mathrm{in}}}{RT}) \end{bmatrix} \\
O = \quad & T\left[Z_{20}B_{20}K_2(T)B_{\mathrm{in}}^{2tr}\mathrm{Exp}(\tfrac{Z_{\mathrm{in}}^{tr}\mu_{\mathrm{in}}}{RT}) + Z_{20}B_{20}K_2(T)B_{20}^{tr}\mathrm{Exp}(\tfrac{Z_{20}^{tr}\mu_{20}+Z_{20}^{'tr}\mu_{\mathrm{in}}}{RT})\right]
\end{aligned}$$

Furthermore, $\hat{\mathcal{R}}$ is a symmetric matrix which can be written as

$$\hat{\mathcal{R}}(\frac{\partial \mathrm{H}}{\partial w}(w)) := \begin{bmatrix} 0 & \cdots & 0 & \\ \vdots & \ddots & \vdots & \mathbf{0}_m \\ 0 & \cdots & 0 & \\ (\mathbf{0}_m)^{tr} & & Y \end{bmatrix} \tag{4.9}$$

Since we have $dU = 0$ for the interconnected network, this implies that

$$Y = \mu_{10}^{tr}M + \mu_{\mathrm{in}}^{tr}N + \mu_{20}^{tr}O$$

Furthermore, we remark that since $dU = \mu^{tr}dx + TdS$, we have

$$\frac{dS}{dt} = \frac{Y}{T^2} \tag{4.10}$$

We will see in Sect. 4.2.3, Y is related to the entropy source term and $Y = \hat{\sigma}T^2$ where $\hat{\sigma}$ is the entropy creation. There will be more discussion about the entropy balance in the next section.

4.2.3 Entropy balance

In this section, we shall relate the port-Hamiltonian formulation of the interconnected chemical reaction network with the second law of thermodynamics. With

this in mind let us compute the time-derivative of the entropy S

$$\begin{aligned}\frac{dS}{dt} &= \frac{\partial^{tr} S(w)}{\partial w}\dot{w} \\ &= \left[-\frac{\mu_{10}^{tr}}{T}, -\frac{\mu_{\text{in}}^{tr}}{T}, -\frac{\mu_{20}^{tr}}{T}, \frac{1}{T}\right] \begin{bmatrix} 0 & \cdots & 0 & M \\ \vdots & \ddots & \vdots & N \\ 0 & \cdots & 0 & O \\ -M^{tr} & -N^{tr} & -O^{tr} & -Y \end{bmatrix} \begin{bmatrix} \frac{\mu_{10}}{T} \\ \frac{\mu_{\text{in}}}{T} \\ \frac{\mu_{20}}{T} \\ -\frac{1}{T} \end{bmatrix} \\ &= \frac{1}{T}\hat{\mu}^{tr} Z L\text{Exp}(\tfrac{Z^{tr}\hat{\mu}}{RT})\end{aligned} \tag{4.11}$$

Denote $\hat{\gamma} = \frac{Z^{tr}\hat{\mu}}{RT}$. It has been shown in (van der Schaft et al. 2013a) (using the properties of the Laplacian matrix L) that for any $\hat{\gamma} \in \mathbb{R}^c$

$$\hat{\gamma}^{tr} L\text{Exp}(\hat{\gamma}) \geqslant 0, \tag{4.12}$$

while $\hat{\gamma}^{tr} L\text{Exp}(\hat{\gamma}) = 0$ if and only if $B^{tr}\hat{\gamma} = 0$. Hence, the entropy balance equation becomes

$$\frac{dS}{dt} = R\hat{\gamma}^{tr} L\text{Exp}(\hat{\gamma}) =: \hat{\sigma} \geqslant 0 \tag{4.13}$$

Here $\hat{\sigma}$ is the irreversible entropy source term. Note that the positivity of the irreversible entropy source term is consistent with the second law of thermodynamics and is due to the positive semi-definiteness of the dissipation matrix $\hat{\mathcal{R}}$ in (4.9). Indeed the only non-zero term of $\hat{\mathcal{R}}$ is the $(m+1, m+1)$th element, denoted as Y, which is related to the entropy source term as

$$Y = \hat{\sigma} T^2 \tag{4.14}$$

and which is in line with equation (4.10). Furthermore, note that the entropy balance in each chemical reaction network can be expressed as the sum of two distinct contributions. One is due to changes in the non-shared species and thus vanishes at equilibrium, while the other is due to the interconnection, see (Rao and Esposito 2016) and (Qian and Beard 2005).

4.2.4 Asymptotic stability

In this section we aim at proving a similar result for the asymptotic stability of the interconnected chemical reaction network based on the port-Hamiltonian formulation in Sect. 3, employing the entropy-based availability function. Firstly, the strict concavity of the total entropy S needs to be proved.

Proposition 4.2. *The total entropy of an interconnected chemical network which is composed of two chemical reaction networks with shared chemical species, given in (4.7), (4.8) and (4.9), is strictly concave.*

Proof. Let S_1 be the entropy of chemical reaction network 1, and S_2 the entropy of chemical reaction network 2. As has been proved in (Callen 1960), for homogeneous mixtures, the entropy function is necessarily concave. Moreover, the entropy is strictly concave if at least one global extensive property (such as volume, total mass, or total mole number) is fixed, see (Alonso and Ydstie 2001) and (Jillson and Ydstie 2007). Thus, since the chemical reaction network is assumed to be isochoric, i.e. $dV = 0$, the entropies $S_1(x_1, T)$ and $S_2(x_2, T)$ are strictly concave. Therefore, we have

$$S_1((1-\alpha)x_1 + \alpha x_1', T) > (1-\alpha)S_1(x_1, T) + \alpha S_1(x_1', T)$$

$$S_2((1-\alpha)x_2 + \alpha x_2', T) > (1-\alpha)S_2(x_2, T) + \alpha S_2(x_2', T)$$

Hence we obtain

$$\begin{aligned} S((1-\alpha)\hat{x} + \alpha\hat{x}', T) &= S_1((1-\alpha)\hat{x} + \alpha\hat{x}', T) + S_2((1-\alpha)\hat{x} + \alpha\hat{x}', T) \\ &= S_1((1-\alpha)x_1 + \alpha x_1', T) + S_2((1-\alpha)x_2 + \alpha x_2', T) \\ &> (1-\alpha)S_1(x_1, T) + \alpha S_1(x_1', T) + (1-\alpha)S_2(x_2, T) \\ &\quad + \alpha S_2(x_2', T) \end{aligned}$$

Collecting the terms, we have $(1-\alpha)S_1(x_1, T) + (1-\alpha)S_2(x_2, T) = (1-\alpha)S(\hat{x}, T)$ and $\alpha S_1(x_1', T) + \alpha S_2(x_2', T) = \alpha S(\hat{x}, T)$. Hence we obtain

$$S((1-\alpha)\hat{x} + \alpha\hat{x}', T) > (1-\alpha)S(\hat{x}, T) + \alpha S(\hat{x}, T)$$

□

Then as before we define the entropy-based availability function as

$$A(w) := -S(w) + S(w^o) + \frac{\partial^{tr} S}{\partial w}(w^o)(w - w^o) \tag{4.15}$$

where $w^o \in \Sigma_T$ is a reference point taken to be a thermodynamic equilibrium.

Theorem 4.3. *Consider the interconnected chemical reaction network given by (4.7), (4.8) and (4.9), with $A : \mathbb{R}_+^{m+1} \to \mathbb{R}$ given by (4.15). Then A has a strict minimum at w^o with $A(w^o) = 0$, while the time-derivative $\frac{dA}{dt}$ is less than or equal to zero with equality only at w^o.*

Proof. By Proposition 4.2, the total entropy of the interconnected chemical reaction network is strict concave and A has a strict minimum at w^o. Moreover, the time derivative of $A(w)$ is given as

$$\begin{aligned}
\tfrac{dA}{dt} &= \tfrac{\partial A}{\partial w}(w)\dot{w} \\
&= -(\tfrac{dS}{dw}(w) - \tfrac{dS}{dw}(w^o))^{tr}\tfrac{dw}{dt} \\
&= -\begin{bmatrix} \frac{(\mu_{10}^o)^{tr}}{T^o} - \frac{(\mu_{10})^{tr}}{T} \\ \frac{(\mu_{\text{in}}^o)^{tr}}{T^o} - \frac{(\mu_{\text{in}})^{tr}}{T} \\ \frac{(\mu_{20}^o)^{tr}}{T^o} - \frac{(\mu_{20})^{tr}}{T} \\ \frac{1}{T} - \frac{1}{T^o} \end{bmatrix}^{tr} \begin{bmatrix} 0 & \cdots & 0 & M \\ \vdots & \ddots & \vdots & N \\ 0 & \cdots & 0 & O \\ -M^{tr} & -N^{tr} & -O^{tr} & -Y \end{bmatrix} \begin{bmatrix} \frac{\mu_{10}}{T} \\ \frac{\mu_{\text{in}}}{T} \\ \frac{\mu_{20}}{T} \\ -\frac{1}{T} \end{bmatrix} \\
&= -(\tfrac{\hat{\mu}^{tr}Z}{T} - \tfrac{(\hat{\mu}^o)^{tr}Z}{T^o})L\text{Exp}(\tfrac{Z^{tr}\hat{\mu}}{RT}) \\
&= -R\hat{\gamma}^{tr}L\text{Exp}(\hat{\gamma}) + R(\hat{\gamma}^o)^{tr}L\text{Exp}(\hat{\gamma})
\end{aligned} \tag{4.16}$$

where $\hat{\mu} = RT\text{Ln}\frac{\hat{x}}{\hat{x}^*}$ is the vector of chemical potentials, $\hat{\mu}^o = RT^o\text{Ln}\frac{\hat{x}^o}{\hat{x}^*}$, $\hat{\gamma} = \frac{Z^{tr}\hat{\mu}}{RT} = Z^{tr}\text{Ln}\frac{\hat{x}}{\hat{x}^*}$ and $\hat{\gamma}^o = \frac{Z^{tr}\hat{\mu}^o}{RT^o} = Z^{tr}\text{Ln}\frac{\hat{x}^o}{\hat{x}^*}$. Since $\hat{x}^*$ and $\hat{x}^o$ are both thermodynamic equilibria, we have

$$C^{tr}\text{Ln}(\hat{x}^o) = C^{tr}\text{Ln}(\hat{x}^*)$$

which is equivalent to

$$C^{tr}\text{Ln}(\frac{\hat{x}^o}{\hat{x}^*}) = (ZB)^{tr}\text{Ln}(\frac{\hat{x}^o}{\hat{x}^*}) = \mathbf{0}_c$$

$$B^{tr}(Z^{tr}\text{Ln}(\frac{\hat{x}^o}{\hat{x}^*})) = B^{tr}\hat{\gamma}^o = \mathbf{0}_c$$

Recall (van der Schaft et al. 2013a) that since L is a balanced weighted Laplacian matrix, for any $\hat{\gamma} \in \mathbb{R}^c$, we have $\hat{\gamma}^{tr}L\text{Exp}(\hat{\gamma}) \geqslant 0$, while $\hat{\gamma}^{tr}L\text{Exp}(\hat{\gamma}) = 0$ if and only if $B^{tr}\hat{\gamma} = 0$. Hence

$$(\hat{\gamma}^o)^{tr}L\text{Exp}(\hat{\gamma}^o) = 0$$

Therefore the time derivative of $A(z)$ satisfies

$$\frac{dA}{dt} = -R\hat{\gamma}^{tr}L\text{Exp}(\hat{\gamma}) \leqslant 0$$

□

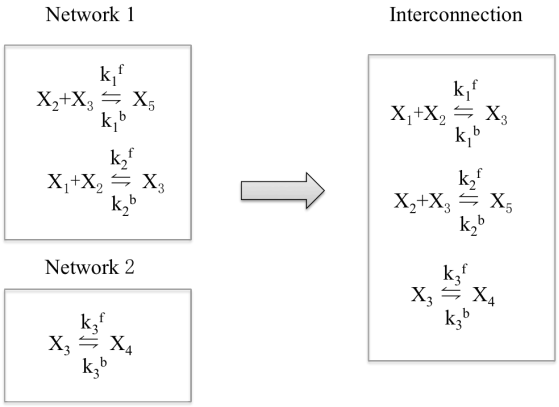

Figure 4.2: Interconnection between two simple chemical reaction networks.

4.2.5 Example: interconnection of two chemical reaction networks

Consider an interconnection of two simple chemical reaction networks, see Figure 4.2. The chemical reaction network 1 is composed of 4 species, denoted as X_1, X_2, X_3 and X_5. Denote the forward/backward chemical reaction rate coefficients as k_1^f, k_1^b for the chemical reaction 1 and k_2^f, k_2^b for the chemical reaction 2. Note that $m_1 = 4$, $r_1 = 2$ and $c_1 = 4$, and let us fix the order of species as X_1, X_2, X_5, X_3, the order of complexes as $X_1 + X_2$, $X_2 + X_3$, X_5, X_3, and the order of the reactions as $X_2 + X_3 \rightleftharpoons X_5$, $X_1 + X_2 \rightleftharpoons X_3$. Then the stoichiometric matrix is $C_1 = \begin{bmatrix} 0 & -1 \\ -1 & -1 \\ 1 & 0 \\ -1 & 1 \end{bmatrix}$, the complex composition matrix is $Z_1 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \end{bmatrix}$, and the incidence matrix is $B_1 = \begin{bmatrix} 0 & -1 \\ -1 & 0 \\ 1 & 0 \\ 0 & 1 \end{bmatrix}$. Define the matrix of conductances $K_1(T)$ as $K_1(T) = \begin{bmatrix} \kappa_1(T) & 0 \\ 0 & \kappa_2(T) \end{bmatrix}$.

The chemical reaction network 2 is composed of 2 species, denoted as X_3 and X_4, and k_3^f and k_3^b are the forward/backward chemical reaction rate coefficient for the chemical reaction 3. Thus $m_2 = 2$, $r_2 = 1$ and $c_2 = 2$. For the modeling, let us fix the order of species as X_3, X_4, and the order of complexes as X_3, X_4.

Then the stoichiometric matrix is $C_2 = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$, the complex composition matrix is $Z_2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ and the incidence matrix is $B_2 = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$. Define the matrix of conductances $K_2(T)$ as $K_2(T) = \kappa_3(T)$.

The shared species between the two chemical reaction networks is X_3, and the shared complex is X_3; thus we have $m_{\text{in}} = 1$ and $c_{\text{in}} = 1$. When the interconnection takes place, the two reactors combine with each other and the shared species X_3 in the two chemical reaction networks can be considered as one species. For the interconnected chemical reaction network, let us order the species as X_1, X_2, X_5, X_3, X_4 (their concentrations are denoted as x_i, $i = 1, \ldots, 5$), the complexes as $X_1 + X_2$, X_5, $X_2 + X_3$, X_3, X_4, and the chemical reactions as $X_1 + X_2 \rightleftharpoons X_3$, $X_2 + X_3 \rightleftharpoons X_5$, $X_3 \rightleftharpoons X_4$. Then for the interconnected chemical reaction network, the incidence matrix is

$$B = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & 0 & 1 \end{bmatrix},$$

the complex composition matrix is

$$Z = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix},$$

the stoichiometric matrix is

$$C = \begin{bmatrix} 0 & -1 & 0 \\ -1 & -1 & 0 \\ 1 & 0 & 0 \\ -1 & 1 & -1 \\ 0 & 0 & 1 \end{bmatrix},$$

while the matrix of conductances is

$$K_1(T) = \begin{bmatrix} \kappa_1(T) & 0 & 0 \\ 0 & \kappa_2(T) & 0 \\ 0 & 0 & \kappa_3(T) \end{bmatrix},$$

with $L = BK(T)B^{tr}$.

Define the state vector $w = [\hat{x}, U]^{tr} = [x_1, x_2, x_5, x_3, x_4, U]^{tr}$ with U the total internal energy, the Hamiltonian function $\mathrm{H} = -S$ with S the total entropy, and the co-state vector $\frac{\partial(-S)}{\partial w} = [\frac{\hat{\mu}}{T}, -\frac{1}{T}]^{tr} = [\frac{\mu_1}{T}, \frac{\mu_2}{T}, \frac{\mu_5}{T}, \frac{\mu_3}{T}, \frac{\mu_4}{T}, -\frac{1}{T}]^{tr}$ with μ_i the chemical potential of ith species, $i = 1, \ldots, 5$ and T the temperature. Then the port-Hamiltonian formulation for the interconnected chemical reaction network shown in Figure 4.2 can be written as

$$\begin{bmatrix} \dot{x_1} \\ \dot{x_2} \\ \dot{x_5} \\ \dot{x_3} \\ \dot{x_4} \\ \dot{U} \end{bmatrix} = \begin{bmatrix} 0 & & \cdots & & 0 & M_1 \\ & \ddots & & & & M_2 \\ \vdots & & 0 & & \vdots & M_3 \\ & & & \ddots & & N_1 \\ 0 & & \cdots & & 0 & O_1 \\ -M_1 & -M_2 & -M_3 & -N_1 & -O_1 & Y \end{bmatrix} \begin{bmatrix} \frac{\mu_1}{T} \\ \frac{\mu_2}{T} \\ \frac{\mu_5}{T} \\ \frac{\mu_3}{T} \\ \frac{\mu_4}{T} \\ -\frac{1}{T} \end{bmatrix} \tag{4.17}$$

where

$$\begin{aligned}
M_1 &= T\kappa_2(T)[\mathrm{Exp}(\tfrac{\mu_1+\mu_2}{RT}) - \mathrm{Exp}(\tfrac{\mu_3}{RT})] \\
M_2 &= T\kappa_2(T)[\mathrm{Exp}(\tfrac{\mu_1+\mu_2}{RT}) - \mathrm{Exp}(\tfrac{\mu_3}{RT})] + T\kappa_1(T)[\mathrm{Exp}(\tfrac{\mu_2+\mu_3}{RT}) - \mathrm{Exp}(\tfrac{\mu_5}{RT})] \\
M_3 &= -T\kappa_1(T)[\mathrm{Exp}(\tfrac{\mu_2+\mu_3}{RT}) - \mathrm{Exp}(\tfrac{\mu_5}{RT})] \\
N_1 &= -T\kappa_2(T)[\mathrm{Exp}(\tfrac{\mu_1+\mu_2}{RT}) - \mathrm{Exp}(\tfrac{\mu_3}{RT})] + T\kappa_1(T)[\mathrm{Exp}(\tfrac{\mu_2+\mu_3}{RT}) - \mathrm{Exp}(\tfrac{\mu_5}{RT})] \\
&\quad -T\kappa_3(T)[\mathrm{Exp}(\tfrac{\mu_3}{RT}) - \mathrm{Exp}(\tfrac{\mu_4}{RT})] \\
O_1 &= T\kappa_3(T)[\mathrm{Exp}(\tfrac{\mu_3}{RT}) - \mathrm{Exp}(\tfrac{\mu_4}{RT})] \\
Y &= \mu_1^{tr}M_1 + \mu_2^{tr}M_2 + \mu_5^{tr}M_3 + \mu_3^{tr}N_1 + \mu_4^{tr}O_1
\end{aligned}$$

4.3 Interconnection arising from port interconnection

In this section, it will be shown that the procedure for interconnection of chemical reaction networks can be also interpreted as arising from power-port interconnection at the boundary shared chemical species, see Figure 4.3. When the two chemical reaction networks connect to each other, there is a transformation of mass and energy between the two reactors: the fluxes of the boundary shared species add up to zero, and the difference of the chemical potentials of the boundary shared species are equal to zero. Thus the interconnection of two chemical reaction networks can be seen to result from the power-port interconnection constraints

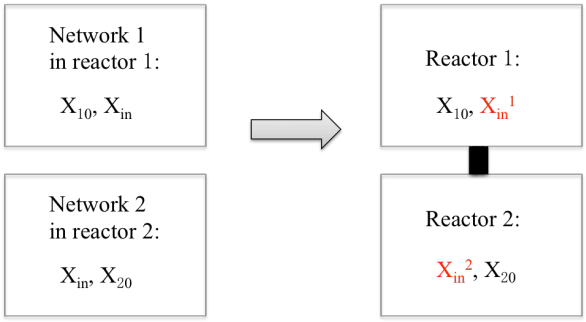

Figure 4.3: Interconnection through shared boundary species.

$$\mu_{b1} = \mu_{b2}$$

$$F_{b1} + F_{b2} = 0$$

with μ_{bi} the chemical potential of the boundary shared species in each chemical reaction network, and F_{bi} the influx/efflux of the boundary shared species in each chemical reaction network, $i = 1, 2$.

In order to simplify the modeling, we assume that the heat transfer between the two reactors is much faster than any reaction time scale, so that the temperatures of two reactor are equal, i.e., $T = T_1 = T_2$. We suppose that only the shared species can transfer between the reactors. Moreover, we suppose that the change of pressure P can be neglected in each reactor and we have $P = P_1 = P_2$ with P constant.

4.3.1 Port-Hamiltonian structure

Let us denote Z_i as the complex composition matrix, B_i as the incidence matrix, C_i the stoichiometric matrix and K_i the matrix of conductances, and finally the Laplacian matrix $L_i = B_i K_i B_i^{tr}$, for each chemical reaction network, $i = 1, 2$.

Let x_i be the state vector, $\mathrm{H}_i = -S_i$ with S_i the entropies, be the Hamiltonian function, and $\frac{\partial \mathrm{H}_i}{\partial x_i} = \frac{\mu_i}{T}$ with μ_i the vector of chemical potentials, be the co-state vector of each chemical reaction network, $i = 1, 2$. Since the temperatures in both reactors are considered to be equal for all time, it is sufficient to consider only mass balance equations, i.e., the dynamics of the concentrations of the species. Then the port-Hamiltonian formulation of each chemical reaction network reduces to (3.6),

$$\begin{aligned}\dot{x_i} &= -Z_i B_i K_i B_i^{tr} \mathrm{Exp}(Z_i^{tr} \mathrm{Ln} \tfrac{x_i}{x_i^*}) \\ &= -Z_i B_i K_i B_i^{tr} \mathrm{Exp}(\tfrac{Z_i^{tr} \mu_i}{RT}) \\ &= -Z_i B_i K_i B_i^{tr} \mathrm{Exp}(\tfrac{Z_i^{tr}}{R} \tfrac{\partial \mathrm{H}}{\partial x})\end{aligned}$$

with $\mu_i = RT\mathrm{Ln}\frac{x_i}{x_i^*}$.

Define the state vector $x = [x_1, x_2]^{tr}$, the Hamiltonian function $\mathrm{H} = -S = -(S_1 + S_2)$, and the co-state vector $\frac{\partial \mathrm{H}}{\partial x} = [\frac{\partial \mathrm{H}}{\partial x_1}, \frac{\partial \mathrm{H}}{\partial x_2}]^{tr} = [\frac{\mu_1}{T}, \frac{\mu_2}{T}]^{tr}$, then the dynamics of the interconnected chemical reaction network can be written as

$$\begin{aligned}\dot{x} &= \begin{bmatrix} \dot{x_1} \\ \dot{x_2} \end{bmatrix} = \begin{bmatrix} -Z_1 B_1 K_1 B_1^{tr} \mathrm{Exp}(\frac{Z_1^{tr}}{R} \frac{\partial \mathrm{H}}{\partial x_1}) \\ -Z_2 B_2 K_2 B_2^{tr} \mathrm{Exp}(\frac{Z_2^{tr}}{R} \frac{\partial \mathrm{H}}{\partial x_2}) \end{bmatrix} + \begin{bmatrix} F_{b1} \\ F_{b2} \end{bmatrix} \\ &= -ZBKB^{tr} \mathrm{Exp}(\tfrac{Z^{tr}}{R} \tfrac{\partial \mathrm{H}}{\partial x}) + G\Lambda \\ &= -ZL\mathrm{Exp}(\tfrac{Z^{tr}}{R} \tfrac{\partial \mathrm{H}}{\partial x}) + G\Lambda\end{aligned} \tag{4.18}$$

$$0 = \mu_{b1} - \mu_{b2} = G^{tr} T \frac{\partial \mathrm{H}}{\partial x} \tag{4.19}$$

where $\Lambda \in \mathbb{R}^k$ is a vector of Lagrange multipliers, $G = \begin{bmatrix} C_b \\ -C_b \end{bmatrix} \in \mathbb{R}^{m \times k}$ is a constant matrix decided by the port interconnection with $F_{b1} = -F_{b2} = C_b\Lambda$, $k \in \mathbb{N}$, $Z = \begin{bmatrix} Z_1 & 0 \\ 0 & Z_2 \end{bmatrix}$ is the complex composition matrix, $B = \begin{bmatrix} B_1 & 0 \\ 0 & B_2 \end{bmatrix}$ is the incidence matrix, and $K = \begin{bmatrix} K_1 & 0 \\ 0 & K_2 \end{bmatrix}$ is the matrix of conductance, $L = BKB^{tr}$.

Here we introduce the methodology in (van der Schaft 2013) to eliminate the mass kinetics and power port constraints in the dynamics (4.18) and (4.19). Assume that the matrix G is a full-rank matrix of rank k. Define a matrix $D \in \mathbb{R}^{m \times (m-k)}$ of rank $m - k$ such that $D^{tr}G = G^{tr}D = 0$.

Define a new vector $z \in \mathbb{R}^m$ such that

$$z = \begin{bmatrix} z_1 \\ z_2 \end{bmatrix} = \begin{bmatrix} D^{tr} \\ G^{tr} \end{bmatrix} x$$

Since the rows of D^{tr} are orthogonal to the rows of G^{tr}, the mapping $x \to z$ is a well-defined coordinate transformation. In the new coordinates z, the dynamics

(4.18) takes the form

$$\begin{aligned}\dot{z} &= \begin{bmatrix} z_1 \\ z_2 \end{bmatrix} = \begin{bmatrix} D^{tr} \\ G^{tr} \end{bmatrix} \dot{x} \\ &= -\begin{bmatrix} D^{tr} \\ G^{tr} \end{bmatrix} ZL\mathrm{Exp}(\tfrac{Z^{tr}}{R}\tfrac{\partial \mathrm{H}}{\partial x}) + \begin{bmatrix} D^{tr} \\ G^{tr} \end{bmatrix} G\Lambda \\ &= -\begin{bmatrix} D^{tr}ZL \\ G^{tr}ZL \end{bmatrix} \mathrm{Exp}\left(\tfrac{Z^{tr}}{R}[D,G]\tfrac{\partial \tilde{\mathrm{H}}}{\partial z}\right) + \begin{bmatrix} 0 \\ G^{tr}G \end{bmatrix} \Lambda \\ &= -\begin{bmatrix} D^{tr}ZL \\ G^{tr}ZL \end{bmatrix} \mathrm{Exp}\left(\tfrac{1}{R}[Z^{tr}D\tfrac{\partial \tilde{\mathrm{H}}}{\partial z_1}, Z^{tr}G\tfrac{\partial \tilde{\mathrm{H}}}{\partial z_2}]\right) + \begin{bmatrix} 0 \\ G^{tr}G \end{bmatrix} \Lambda\end{aligned} \tag{4.20}$$

with $\tilde{\mathrm{H}}$ the Hamiltonian function expressed in the new coordinates z.

From (4.19), we obtain

$$0 = G^{tr}T\frac{\partial \mathrm{H}}{\partial x} = G^{tr}T[D,G]\frac{\partial \tilde{\mathrm{H}}}{\partial z} = T[0, G^{tr}G]\frac{\partial \tilde{\mathrm{H}}}{\partial z} \tag{4.21}$$

which is equivalent to

$$G^{tr}G\frac{\partial \tilde{\mathrm{H}}}{\partial z_2} = 0 \tag{4.22}$$

Since the matrix $G^{tr}G$ is invertible, this implies that $\frac{\partial \tilde{\mathrm{H}}}{\partial z_2} = 0$. Then the equation (4.20) becomes

$$\dot{z} = \begin{bmatrix} z_1 \\ z_2 \end{bmatrix} = -\begin{bmatrix} D^{tr}ZL \\ G^{tr}ZL \end{bmatrix} \mathrm{Exp}\left(\frac{Z^{tr}D}{R}\frac{\partial \tilde{\mathrm{H}}}{\partial z_1}\right) + \begin{bmatrix} 0 \\ G^{tr}G \end{bmatrix} \Lambda \tag{4.23}$$

Since in (4.23), Λ only influences the z_2-dynamics, the constrained dynamics is determined only by the z_1-dynamics. Therefore the dynamics reduces to the form

$$\dot{z_1} = \tilde{Z}BKB^{tr}\mathrm{Exp}(\frac{\tilde{Z}}{R}\frac{\partial \tilde{\mathrm{H}}}{\partial z_1}) \tag{4.24}$$

with $\tilde{Z} = D^{tr}Z$. After elimination of the constraint of equal chemical potentials of the shared species, the equation (4.24) can thus be seen to result in the dynamics (4.5) in the previous section.

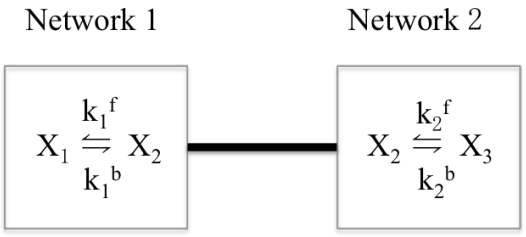

Figure 4.4: Port interconnection between two isothermal chemical reaction networks.

4.3.2 Example: interconnection of two isothermal chemical reaction networks

Consider an interconnection of two chemical reaction networks, see Figure 4.4. The chemical reaction network 1 is composed of 2 species, denoted as X_1 and X_2, with k_1^f and k_1^b the forward/backward chemical reaction rate coefficients. Thus we have $m_1 = 2$, $r_1 = 1$ and $c_1 = 2$. The chemical reaction network 2 is composed of 2 species, denoted as X_2 and X_3, with k_2^f and k_2^b are the forward/backward chemical reaction rate coefficients. Hence we have $m_2 = 2$, $r_2 = 1$ and $c_2 = 2$. The interconnection takes place when the two chemical reactor are connected to each other by a tube, and we assume that only the species X_2 can pass through this tube.

Denote the complex composition matrix of each chemical reaction network as Z_1 and Z_2, with $Z_1 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ and $Z_2 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$; denote the incidence matrix of each chemical reaction network by B_1 and B_2, with $B_1 = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$ and $B_2 = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$; denote the matrix of conductances of each network as K_1 and K_2, with $K_1 = \kappa_1 \in \mathbb{R}_+$ and $K_2 = \kappa_2 \in \mathbb{R}_+$; denote the concentrations of X_1 and X_2 in the chemical reaction network 1 as x_1^1 and x_2^1, the state vector $x_1 = [x_1^1, x_2^1]^{tr}$, and the concentrations of X_2 and X_3 in the chemical reaction network 2 as x_2^2 and x_3^2, the state vector $x_2 = [x_2^2, x_3^2]^{tr}$. Then the dynamics of the interconnected chemical

reaction network can be written as

$$\begin{aligned}\begin{bmatrix} \dot{x}_1^1 \\ \dot{x}_2^1 \\ \dot{x}_2^2 \\ \dot{x}_3^2 \end{bmatrix} &= \begin{bmatrix} -Z_1 B_1 K_1 B_1^{tr} & 0 \\ 0 & -Z_2 B_2 K_2 B_2^{tr} \end{bmatrix} \begin{bmatrix} \mathrm{Exp}(Z_1^{tr} \mathrm{Ln} \frac{x_1}{x_1^*}) \\ \mathrm{Exp}(Z_2^{tr} \mathrm{Ln} \frac{x_2}{x_2^*}) \end{bmatrix} + G\Lambda \\ &= -\begin{bmatrix} \kappa_1 & -\kappa_1 & 0 & 0 \\ -\kappa_1 & \kappa_1 & 0 & 0 \\ 0 & 0 & \kappa_2 & -\kappa_2 \\ 0 & 0 & -\kappa_2 & \kappa_2 \end{bmatrix} \begin{bmatrix} \frac{x_1^1}{x_1^{1*}} \\ \frac{x_2^1}{x_2^{1*}} \\ \frac{x_2^2}{x_2^{2*}} \\ \frac{x_3^2}{x_3^{2*}} \end{bmatrix} + \begin{bmatrix} 0 \\ 1 \\ -1 \\ 0 \end{bmatrix} \Lambda \end{aligned} \tag{4.25}$$

where $G = [0, 1, -1, 0]^{tr}$, $G\Lambda$ is the vector of boundary flux between the two chemical reaction networks. The constraint of equal chemical potential of the shared species X_2 is

$$\mu_2^1 = \mu_2^2 \tag{4.26}$$

which can be rewritten as

$$\mathrm{Ln} \frac{x_2^1}{x_2^{1*}} = \mathrm{Ln} \frac{x_2^2}{x_2^{2*}} \tag{4.27}$$

This is equivalent to

$$\frac{x_2^1}{x_2^{1*}} = \frac{x_2^2}{x_2^{2*}} \tag{4.28}$$

and thus the power port constraint can be simply written as

$$0 = G^{tr} T \frac{\partial \mathrm{H}}{\partial x} = G^{tr} RT \mathrm{Ln} \frac{x}{x^*} \tag{4.29}$$

A matrix $D \in \mathbb{R}^{4\times 3}$ of rank 3 such that $D^{tr}G = G^{tr}D = 0$ is given by

$$D = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{4.30}$$

Define the new state vector $z = \begin{bmatrix} z_1 \\ z_2 \end{bmatrix} = \begin{bmatrix} D^{tr} \\ G^{tr} \end{bmatrix} x = \begin{bmatrix} x_1^1 \\ x_2^1 + x_2^2 \\ x_3^2 \\ x_2^1 - x_2^2 \end{bmatrix}$. It can be checked that the mapping $x \to z$ is a well-defined coordinate transformation. The dynamics (4.25) in the z-coordinates takes the form

$$\begin{aligned}
\dot{z} &= \begin{bmatrix} D^{tr} \\ G^{tr} \end{bmatrix} \dot{x} \\
&= -\begin{bmatrix} D^{tr} \\ G^{tr} \end{bmatrix} \begin{bmatrix} \kappa_1 & -\kappa_1 & 0 & 0 \\ -\kappa_1 & \kappa_1 & 0 & 0 \\ 0 & 0 & \kappa_2 & -\kappa_2 \\ 0 & 0 & -\kappa_2 & \kappa_2 \end{bmatrix} \mathrm{Exp}\left(\tfrac{1}{R}\tfrac{\partial \mathrm{H}}{\partial x}\right) + \begin{bmatrix} D^{tr} \\ G^{tr} \end{bmatrix} G\Lambda \\
&= -\begin{bmatrix} D^{tr} \\ G^{tr} \end{bmatrix} \begin{bmatrix} \kappa_1 & -\kappa_1 & 0 & 0 \\ -\kappa_1 & \kappa_1 & 0 & 0 \\ 0 & 0 & \kappa_2 & -\kappa_2 \\ 0 & 0 & -\kappa_2 & \kappa_2 \end{bmatrix} \mathrm{Exp}\left(\tfrac{1}{R}[D,G]\tfrac{\partial \tilde{\mathrm{H}}}{\partial z}\right) + \begin{bmatrix} 0 \\ G^{tr}G \end{bmatrix} \Lambda \\
&= -\begin{bmatrix} \kappa_1 & -\kappa_1 & 0 & 0 \\ -\kappa_1 & \kappa_1 & \kappa_2 & -\kappa_2 \\ 0 & 0 & -\kappa_2 & \kappa_2 \\ -\kappa_1 & \kappa_1 & -\kappa_2 & \kappa_2 \end{bmatrix} \mathrm{Exp}\left(\tfrac{1}{R}\left[D\tfrac{\partial \tilde{\mathrm{H}}}{\partial z_1}, G\tfrac{\partial \tilde{\mathrm{H}}}{\partial z_2}\right]\right) + \begin{bmatrix} 0 \\ 0 \\ 0 \\ 2 \end{bmatrix} \Lambda
\end{aligned} \tag{4.31}$$

The constraint (4.29) can be rewritten as

$$\begin{aligned}
0 &= G^{tr}T\tfrac{\partial \mathrm{H}}{\partial x} = G^{tr}T[D,G]\tfrac{\partial \tilde{\mathrm{H}}}{\partial z} \\
&= T[0, G^{tr}G]\tfrac{\partial \tilde{\mathrm{H}}}{\partial z} = T[0,2]\begin{bmatrix} \frac{\partial \tilde{\mathrm{H}}}{\partial z_1} \\ \frac{\partial \tilde{\mathrm{H}}}{\partial z_2} \end{bmatrix}
\end{aligned} \tag{4.32}$$

which is equivalent to

$$\frac{\partial \tilde{\mathrm{H}}}{\partial z_2} = 0 \tag{4.33}$$

Since the boundary flux Λ only influences the z_2-dynamics, the constrained dynamics is determined only by the z_1-dynamics. Hence the system reduces to

$$\dot{z}_1 = -\begin{bmatrix} \kappa_1 & -\kappa_1 & 0 \\ -\kappa_1 & \kappa_1 & \kappa_2 \\ 0 & 0 & -\kappa_2 \end{bmatrix} \mathrm{Exp}\left(\frac{D}{R}\frac{\partial \tilde{\mathrm{H}}}{\partial z_1}\right) \tag{4.34}$$

It is easy to verify that we will obtain exactly the same formulation if we use the modeling approach in Sect. 4.2.2.

4.4 Conclusion

In this chapter, we offer two different modeling approaches for the interconnection of chemical reaction networks in quasi port-Hamiltonian form. The main difference of the two approaches is the different view on the shared species. Considering the interconnection of the two chemical reaction networks, the assumption made in Sect. 4.2 is that the shared species become the same species, while the starting point of Sect. 4.3 is that there is an inflow and outflow between them. We have proved that both approaches lead to the same result, and thus we can choose one of the two modeling approaches according to the specific physical structure of the systems under consideration.

Chapter 5

Stabilization of control contact systems

5.1 Introduction

It is well-known that the geometric structure of irreversible thermodynamic systems is based on Gibbs' fundamental equation. The canonical differential-geometric structure underlying Gibbs' relation is called contact structure (Arnold 1989, Eberard et al. 2007, Libermann and Marle 1987). The control input-output contact systems which have been proposed in (Eberard et al. 2007), are one of the geometric representations of those thermodynamic systems. Today, some necessary conditions for the stability of the linearisation of contact vector fields are given in (Favache et al. 2009) and a new framework of conservative controlled contact systems has been recently proposed in (Ramirez, Maschke and Sbarbaro 2013a), where the state and co-state variables are considered as independent variables. However, any state feedback (except the trivial constant one) does not preserve the contact structure in closed-loop and thus the closed-loop contact system is no longer a contact system. To cope with this challenge, Ramirez et al. proposed a modified contact form in (Ramirez 2012). By adding the exterior derivative of a function F which fulfills the condition that it does not depend on the coordinate associated to the Reeb vector field, it turns out to be possible to keep the contact structure preserved, in the application of the IDA-PBC method (Ortega et al. 2002).

The problem remains in the study of stability and stabilization for the control input-output contact system. Favache analyzed the stability of the restriction of contact vector fields to certain invariant Legendre submanifolds at equilibrium points in her thesis and later, Ramirez proposed a class of structure-preserving state feedback to keep the closed-loop contact system conservative and proved that the linearization of a contact vector field at equilibrium points has at most n stable eigenvalues when the manifold has dimension $2n + 1$. Therefore, in this chapter, a series of control designs will be proposed in order to add some constraints while choosing the

structure-preserving state feedback and to determine the stable invariant Legendre submanifold on which the closed-loop contact system is partially stable. Using an analogous methodology, see (Kotyczka 2013), the control synthesis of the structure-preserving state feedback will be analyzed through the local study of the linearization of the closed-loop contact system at an equilibrium point and through the discussion of the restriction of the desired Hamiltonian function which generates the stable invariant Legendre submanifold.

The chapter is organized as follows. In Sect. 5.2, we recall the definition of contact systems; in Sect. 5.3, the control synthesis is proposed; and in Sect. 5.4 and 5.5 we apply the previous concepts to two simple thermodynamic models, namely the heat exchanger and a simple isothermal chemical reaction.

5.2 Structure-preserving feedback of controlled contact system

In this section, we review some notations and definitions from contact system as can be found in (Libermann and Marle 2012), (Eberard et al. 2007) and (Favache et al. 2010).

5.2.1 Controlled contact system

Control contact systems are generalizations of Hamiltonian systems adapted to irreversible Thermodynamical systems. They have been defined and their system-theoretical and some control properties have been studied in detail, see (Eberard 2006), (Favache et al. 2009) and (Ramirez 2012). Defined by $n+1$ extensive variables and n intensive variables, contact systems are defined on a thermodynamic phase space endowed with a contact geometry. In the sequel we recall briefly some notations and definitions that are used in this chapter and refer to (Libermann and Marle 1987) for the precise mathematical definitions. First, we start from the definition of *contact manifold*, *contact form*, *contact vector field*, and the *Reeb vector field*.

Definition 5.1. A contact structure on $\mathcal{M}$ is defined by a 1-form θ of class $(2n+1)$ satisfying $\theta \wedge (d\theta)^n \neq 0$, where $\wedge$ denotes the wedge product. θ is called a contact form and the pair $(\mathcal{M}, \theta)$ is called a contact manifold.

According to *Darboux's theorem* for *Pfaffian forms* of constant class, there exists a set of *canonical coordinates* $(x_0, x, p) \in \mathbb{R}^{1\times n\times n}$ which the contact form θ takes the form

$$\theta = dx_0 - \sum_{i=1}^{n} p_i dx_i$$

Definition 5.2. The Reeb vector field E associated with the contact form θ which is the unique vector field satisfying $i_E\theta = 1$ and $i_E d\theta = 0$, where i_E denotes the contraction by the vector field E.

In canonical coordinates, the Reeb vector field is expressed as $E = \frac{\partial}{\partial x_0}$.

Definition 5.3. A vector field X on the contact manifold $(\mathcal{M}, \theta)$ is a contact vector field if and only if there exists a smooth function $\rho \in \mathbb{C}^\infty(\mathcal{M})$ such that

$$L_X\theta = \rho\theta$$

where L_X denotes the Lie derivative with respect to the vector field X.

Every contact vector field can be generated by a *contact Hamiltonian* K and conversely. In a set of canonical coordinates $(x_0, x, p) \in \mathbb{R}^{1\times n\times n}$, the contact vector field corresponding to contact Hamiltonian K can be expressed as

$$X_{\mathrm{K}} = \begin{bmatrix} \mathrm{K} \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} 0 & 0 & -p^{tr} \\ 0 & 0 & -I_n \\ p & I_n & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial \mathrm{K}}{\partial x_0} \\ \frac{\partial \mathrm{K}}{\partial x} \\ \frac{\partial \mathrm{K}}{\partial p} \end{bmatrix} \tag{5.1}$$

where I_n denotes the identity matrix of order n.

By using these definitions, control contact systems are defined as follows (Ramirez 2012).

Definition 5.4. A control contact system affine in the scalar input $u(t)$ is defined by two functions $\mathrm{K}_0 \in C^\infty(\mathcal{M})$ and $\mathrm{K}_c \in C^\infty(\mathcal{M})$, with dynamics

$$\frac{d\tilde{x}}{dt} = X_{K_0} + X_{K_c}u$$

where K_0 is called internal contact Hamiltonian, and K_c is called the *interaction contact Hamiltonian*.

In the sequel we shall only consider contact Hamiltonians that are invariant for the Reeb vector field. That is, in canonical coordinates, they do not depend on the x_0 coordinate.

5.2.2 Structure-preserving feedback

In this section we will recall some results on structure-preserving state feedbacks $u = \alpha(x)$, as shown in (Ramırez et al. 2011). It is shown that there exists a class of state feedback such that the closed-loop contact system is a contact system, however with respect to a modified contact structure. This modified contact structure is defined with respect to modified contact form which is expressed as

$$\theta_d = \theta + dF \tag{5.2}$$

where dF is the differential of a function which is invariant for the Reeb vector field. The associated feedback $\alpha \in C^\infty(\mathcal{M})$ may be written as

$$\alpha(x,p) = \Phi^{'} \circ \mathrm{K}_c \tag{5.3}$$

for some functions $\Phi \in C^\infty(\mathbb{R})$. The closed-loop system is defined by vector field $\hat{X}_{\mathrm{K}}$ defined as

$$\begin{aligned} \hat{X}_{\mathrm{K}} &= X_{\mathrm{K}_0} + \alpha X_{\mathrm{K}_c} \\ &= X_{\mathrm{K}_0} + (\Phi^{'} \circ \mathrm{K}_c) X_{\mathrm{K}_c} \end{aligned} \tag{5.4}$$

This is a contact vector field generated with respect to the modified contact form θ_d and the shaped contact Hamiltonian $\hat{\mathrm{K}}$

$$\hat{\mathrm{K}} = \mathrm{K}_0 + \Phi \circ \mathrm{K}_c + c_F \tag{5.5}$$

where $c_F \in \mathbb{R}$ is a constant. In this dissertation, we assume that the contact Hamiltonian $\hat{\mathrm{K}}$ is *strict*, i.e., the contact vector field $\hat{X}_{\mathrm{K}}$ does not depend on the coordinate x_0.

5.3 Stabilization of the closed-loop contact systems

The structure-preserving feedback introduced in (Ramirez 2012), may only achieve partial stability with respect to a Legendre submanifold of the closed-loop contact form $\theta_d = \theta + dF$. In this section we elaborate on this partial stabilization problem step by step, by showing how to determine the conditions of equilibria, how to choose the function Φ defining the structure-preserving feedback $\alpha(x,p)$ as in (5.3), and thus how to express the stable Legendre submanifold in order to stabilize the closed-loop contact systems.

5.3.1 Equilibrium

In this subsection, we analyze the equilibrium conditions of the closed-loop contact vector field (5.4) with shaped Hamiltonian (5.5) and with respect to the function Φ defining the feedback $\alpha = \Phi'$ in equation (5.3). Let us first recall the characterization of equilibrium points for the closed-loop contact vector field. (x_0^*, x^*, p^*) is an equilibrium point of the closed-loop contact vector field $X_{\mathrm{K}} = X_{\mathrm{K}_0} + \alpha X_{\mathrm{K}_c}$ with contact Hamiltonian $\hat{\mathrm{K}}$ given by (5.5) if and only if the three following conditions are fulfilled (Favache et al. 2009):

$$\hat{\mathrm{K}} \mid_{(x_0^*, x^*, p^*)} = 0 \tag{5.6}$$

$$\frac{\partial \hat{\mathrm{K}}}{\partial p} \mid_{(x_0^*, x^*, p^*)} = 0 \tag{5.7}$$

$$\frac{\partial \hat{\mathrm{K}}}{\partial x} \mid_{(x_0^*, x^*, p^*)} = -p^* \frac{\partial \hat{\mathrm{K}}}{\partial x_0} \mid_{(x_0^*, x^*, p^*)} \tag{5.8}$$

Using the fact that the internal Hamiltonian K_0 and the control Hamiltonian function K_c are invariant for the Reeb vector field, these conditions are equivalent to

$$\left(\mathrm{K}_0 + (\Phi \circ \mathrm{K}_c)\, \mathrm{K}_c\right) \mid_{(x_0^*, x^*, p^*)} = 0 \tag{5.9}$$

$$\left(\frac{\partial \mathrm{K}_0}{\partial p} + \frac{\partial \mathrm{K}_c}{\partial p} \left(\Phi' \circ \mathrm{K}_c\right)\right) \mid_{(x_0^*, x^*, p^*)} = 0 \tag{5.10}$$

$$\left(\frac{\partial \mathrm{K}_0}{\partial x} + \frac{\partial \mathrm{K}_c}{\partial x} (\Phi' \circ \mathrm{K}_c)\right) \mid_{(x_0^*, x^*, p^*)} = 0 \tag{5.11}$$

Remark 5.5. Note that the equation (5.9) implies

$$\Phi \circ \mathrm{K}_c \mid_{(x_0^*, x^*, p^*)} = \left[-\mathrm{K}_0 \cdot (\mathrm{K}_c)^{-1}\right] \mid_{(x_0^*, x^*, p^*)}$$

as long as $\mathrm{K}_c(x_0^*, x^*, p^*) \neq 0$. Furthermore, note that if the equilibrium of the closed-loop contact system is also an equilibrium of the open-loop contact system, this implies that the Hamiltonian function K_0 and the shaped contact Hamiltonian $\hat{\mathrm{K}}$ both satisfy the equations (5.6), (5.7) and (5.8), thus the equilibrium conditions of closed-loop contact systems are satisfied if $\Phi \circ \mathrm{K}_c \mid_{(x_0^*, x^*, p^*)} = 0$ and $\Phi' \circ \mathrm{K}_c \mid_{(x_0^*, x^*, p^*)} = 0$.

5.3.2 The Jacobian matrix $D\hat{X}_{\mathrm{K}}$ of the closed-loop contact vector field $\hat{X}_{\mathrm{K}}$

In this subsection, we shall express the Jacobian matrix $D\hat{X}_{\mathrm{K}}$ in terms of the function Φ defining the structure-preserving feedback α in (5.3). Then we may use the Root locus method and look for the closed-loop poles of the system in order to determine local stability of the contact system.

Consider a closed-loop contact vector field $\hat{X}_{\mathrm{K}} = X_{\mathrm{K}_0} + \alpha X_{\mathrm{K}_c}$ which is generated by a shaped contact Hamiltonian function $\hat{\mathrm{K}} = \mathrm{K}_0 + \Phi \circ \mathrm{K}_c + c_F$ in the canonical coordinates (x_0, x, p). Since $\hat{\mathrm{K}}$ is strict, it has been proven in (Ramirez 2012, chap.4) that for a strict shaped contact vector field $\hat{X}_{\mathrm{K}}$ of the closed-loop contact system, the Jacobian matrix $D\hat{X}_{\mathrm{K}}$ has one eigenvalue 0 and $2n$ non-zero eigenvalues which are symmetrical with respect to the imaginary axis.

Therefore, in canonical coordinates (x_0, x, p), the Jacobian matrix of the closed-loop contact vector field can be written as

$$D\hat{X}_{\mathrm{K}} = \frac{\partial \hat{X}_{\mathrm{K}}}{\partial(x_0, x, p)} = DX_{\mathrm{K}_0} + D\left(\alpha X_{\mathrm{K}_c}\right) = DX_{\mathrm{K}_0} + D\left[(\Phi^{'} \circ \mathrm{K}_c) X_{\mathrm{K}_c}\right] \quad (5.12)$$

where

$$D\left((\Phi^{'} \circ \mathrm{K}_c) X_{\mathrm{K}_c}\right) = DX_{\mathrm{K}_c} \cdot (\Phi^{'} \circ \mathrm{K}_c) + \Phi^{''} \cdot \frac{\partial^{tr} \mathrm{K}_c}{\partial x} \cdot X_{\mathrm{K}_C}$$

We observe that the Jacobian matrix $D\hat{X}_{\mathrm{K}}$ depends on K_0, K_c, $\Phi^{'}(x_0^*, x^*, p^*)$ and $\Phi^{''}(x_0^*, x^*, p^*)$. Actually, we can get some informations about the value of $\Phi^{'}(x_0^*, x^*, p^*)$ by the equilibrium condition (5.9), (5.10), and (5.11) in Sec. 5.3.1. Hence the second derivative of Φ, instead of $\Phi(x_0^*, x^*, p^*)$ and $\Phi'(x_0^*, x^*, p^*)$, determines the poles of $D\hat{X}_{\mathrm{K}}$.

This resembles the Root Locus method to determine the dynamic behavior of closed-loop contact system by changing the output gain, that is to say, the value of $\left(\Phi^{''} \circ K_C\right)(x_0^\star, x^\star, p^\star)$. We know that one of the poles is zero, i.e., $\delta_0 = 0$, and that the remaining $2n$ poles can be written as $\delta_{\pm i} = \pm r_i e^{i\theta}$, $i = 1, \ldots, n$. Then the determinant of Jacobian matrix of the closed-loop contact vector field can be rewritten as

$$\det(\delta I_{2n+1} - D\hat{X}_{\mathrm{K}}) = \delta \prod_{i=1}^{n} (\delta - \delta_{\pm i}) = \delta \prod_{i=1}^{n} (\delta \pm r_i e^{i\theta}) \quad (5.13)$$

Now, the poles of the contact system can be determined by comparing the two expressions of $D\hat{X}_{\mathrm{K}}$ given by (5.12) and (5.13).

5.3.3 Computation of the stable Legendre submanifold

In this section, a stable submanifold Legendre will be built for the partial stabilization of the closed-loop contact system.

Indeed, according to the stable manifold theorem (Marle 2003), for every contact vector field, there exists a *unique* submanifold of the contact manifold, which is invariant generated by the contact form and with respect to this vector field, tangent at the equilibrium point, to a stable linear subspace. Normally, since the shaped contact form θ_d is different form θ and thus $\hat{X}_{\mathrm{K}}$ is different from the unshaped vector field, $\mathcal{L}_{Ud}$ generated by θ_d is different from the one generated by θ. Moreover, it is of interest to check the invariance condition of $\mathcal{L}_{Ud}$ generated by θ_d, because for a thermodynamic system, $\mathcal{L}_{Ud}$ is generated by the internal energy U_d of the system. That is to say, we can shape the internal energy of the system U_d, and even the stability properties of the system, through shaping the Legendre submanifold $\mathcal{L}_{Ud}$ generated by θ_d.

By considering under which condition the obtained closed-loop contact system is also *conservative*, one asks for the closed-loop contact vector field leaving invariant some Legendre submanifold $\mathcal{L}_d$. This is satisfied if and only if (Ramirez 2012, Page 56)

$$\mathrm{K}_0(x,p)\mid_{\mathcal{L}_d} + \Phi \circ \mathrm{K}_c(x,p)\mid_{\mathcal{L}_d} = -c_F \tag{5.14}$$

Interestingly, the closed-loop contact system leaves the Legendre submanifold L_{U_d} invariant, which is derived from a desired function $U_d(x)$. In canonical coordinates (x_0, x, p), this Legendre submanifold is given as

$$L_{Ud} : \begin{cases} x_0^d &= U_d(x) \\ x &= x \\ p^d &= \frac{\partial U_d}{\partial x}(x) \end{cases}$$

Using this expression, the equation (5.14) can be rewritten as

$$\mathrm{K}_0(x, \frac{\partial U_d}{\partial x}(x)) + \Phi \circ \mathrm{K}_c(x, \frac{\partial U_d}{\partial x}(x)) = -c_F \tag{5.15}$$

This condition turns out to be an equation for $U_d(x)$, which is a first-order partial differential equation. To solve this equation for $U_d(x)$, the initial condition of $U_d(x)$ is required, which is provided by the closed-loop equilibrium conditions given in (5.6), (5.7) and (5.8) in Sect. 5.3.1. Now we have to investigate the uniqueness of the solution of equation (5.15). Since the equation (5.15) is generally non-linear, there

could exist multiple solutions if it is solvable. Note that by the center manifold theorem, it follows that for a hyperbolic equilibrium point, there exists unique stable and one unstable submanifolds of dimension n which are both Legendre submanifolds. Moreover, at the equilibrium point, the invariant Legendre submanifold is tangent to a stable linear subspace denoted as Π^{-}. This tangent relation could offer us some restrictions on the $\frac{dU_d}{dx}(x^*)$ which enable us to remove invalid solutions for equation (5.15).

5.3.4 Lyapunov function and availability function

So far we have found the invariant Legendre submanifold on which the closed-loop contact system is partially stable. In this section, we will analyze the global asymptotic stability of closed-loop contact system on the invariant Legendre submanifold and Lyapunov's direct method will be exploited.

Recall the conditions for a Lyapunov function under the assumption that the Lyapunov function depends only on x (Ramirez 2012). Consider a contact manifold $(\mathcal{M}, \theta_d)$ and a set of canonical coordinates (x_0', x, p), a contact vector field $\hat{X}_{\mathrm{K}} = X_{\mathrm{K}_0} + (\Phi^{'} \circ \mathrm{K}_c) X_{\mathrm{K}_c}$, with strict contact Hamiltonian $\hat{\mathrm{K}} = \mathrm{K}_0 + \Phi \circ \mathrm{K}_c$, a Legendre submanifold $L \subset \mathcal{M}$ solving the Pfaffian equation $\theta_d = 0$, an initial state $(x_0'(0), x(0), p(0)) \in \mathcal{L}$, and the equilibrium state $(x_0^{'*}, x^*, p^*) \in \mathcal{L}$ of X. Let $V(x,p) : \mathcal{M} \to \mathbb{R}$ be a continuously differentiable function on $\mathcal{M}$ such that

$$V(x^*) = 0 \tag{5.16}$$

$$V(x) \mid_{\mathcal{L}} > 0, , \forall (x_0, x, p) \mid_{\mathcal{L}} \in \{\mathcal{L} - (x_0^*, x^*, p^*)\} \tag{5.17}$$

$$\frac{dV}{dt} = -\frac{\partial \mathrm{K}_0}{\partial p}\frac{\partial V}{\partial x} \mid_{\mathcal{L}} + \frac{\partial \mathrm{K}_0}{\partial p}\frac{\partial V}{\partial x} \mid_{\mathcal{L}} (\Phi^{'} \circ \mathrm{K}_c) \mid_{\mathcal{L}} < 0, \forall (x_0, x, p) \in \{\mathcal{L} - (x_0^*, x^*, p^*)\} \tag{5.18}$$

Then $(x_0, x, p) = (x_0^*, x^*, p^*)$ is an asymptotically stable equilibrium. Let us define an availability function, based on the desired Hamiltonian function U_d, as a Lyapunov function candidate, and as

$$A(x) = U_d(x) - U_d(x^*) - k^{tr}(x - x^*) \tag{5.19}$$

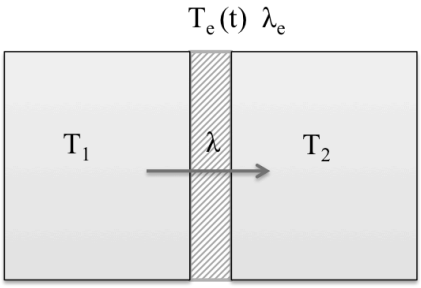

Figure 5.1: Two thermodynamic systems interacting through a conducting wall.

where $k = \frac{\partial U_d}{\partial x}(x^*)$. We know, from Sect. 5.3.3, that the desired contact Hamiltonian U_d is shaped from the shaping of the contact from θ_d and thus from the structure-preserving feedback. Therefore, we need to check if the desired Hamiltonian function obtained from equation (5.15) makes the availability function (5.19) satisfy the conditions (5.16), (5.17), and (5.18).

It follows that the time derivative of A can be written as

$$\begin{aligned}
\tfrac{dA}{dt} &= (\tfrac{\partial U_d}{\partial x}(x) - \tfrac{\partial U_d}{\partial x}(x^*))^{tr}\tfrac{dx}{dt} \\
&= \left(\tfrac{\partial U}{\partial x}(x) - \tfrac{\partial U}{\partial x}(x^*)\right)^{tr}\left[\mathcal{R}\mathcal{J}\tfrac{\partial U}{\partial x}(x) + g(x,u)\right] \\
&= -\tfrac{\partial U}{\partial x}(x^*)\mathcal{R}\mathcal{J}\tfrac{\partial U}{\partial x}(x) + \left(\tfrac{\partial U}{\partial x}(x) - \tfrac{\partial U}{\partial x}(x^*)\right)^{tr} g(x,u) \\
&= -\gamma\tfrac{\partial U}{\partial x}(x^*)\mathcal{J}\tfrac{\partial U}{\partial x}(x)\{S,U\}_{\mathcal{J}} + \left(\tfrac{\partial U}{\partial x}(x) - \tfrac{\partial U}{\partial x}(x^*)\right)^{tr} g(x,u)
\end{aligned} \tag{5.20}$$

Therefore, if the structure-preserving state feedback has been well chosen, in order that A is a Lyapunov function, it suffices to prove that the right-hand side of equation (5.20) is less than or equal to zero.

5.4 Example I: the heat exchanger

Consider two simple thermodynamic systems, indexed by 1 and 2, which interact through a conducting wall, given in Figure 5.1. The dynamics of the interconnected system can be written as the following equation:

$$\begin{bmatrix} \dot{S}_1 \\ \dot{S}_2 \end{bmatrix} = \lambda\left(\frac{1}{\frac{\partial U}{\partial S_2}} - \frac{1}{\frac{\partial U}{\partial S_1}}\right)\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} \frac{\partial U}{\partial S_1} \\ \frac{\partial U}{\partial S_2} \end{bmatrix} + \lambda_e\begin{bmatrix} 0 \\ \frac{1}{\frac{\partial U}{\partial S_2}} - \frac{1}{u} \end{bmatrix} u$$

where S_1 and S_2 are the entropies of subsystem 1 and 2, with $\lambda \in \mathbb{R}$ and $\lambda_e \in \mathbb{R}$ denoting Fourier's heat conduction coefficients of the interacting wall and of the external environment. $U(S_1, S_2) = U_1(S_1) + U_2(S_2)$ is the internal energy of the overall system, which is the sum of the internal energy of each subsystem denoted as $U_1(S_1)$ and $U_2(S_2)$. Furthermore, $u(t)$ represents an external heat source which is the controll input, and $T_e(t) \in \mathbb{R}_+$ is a time dependent external heat source. This heat exchanger system can be written as an irreversible port-Hamiltonian system given by (2.12) in Sect. 2.3, that is,

$$\dot{x} = \mathcal{R}(x, \frac{\partial U}{\partial x}(x))\mathcal{J}\frac{\partial U}{\partial x}(x) + W(x, \frac{\partial U}{\partial x}) + g(\frac{\partial U}{\partial x})u(t)$$

As follows, define the state vector $x = [S_1, S_2]^{tr}$, the Hamiltonian function $\mathrm{H} = U(S_1, S_2)$ and the co-state vector $\frac{\partial U}{\partial x} = [\frac{\partial U}{\partial x_1}, \frac{\partial U}{\partial x_2}]^{tr} = [T_1, T_2]^{tr}$. Furthermore, define the modulating function as follows:

$$\mathcal{R}(x, \frac{\partial U}{\partial x}) = \lambda(\frac{1}{T_2} - \frac{1}{T_1}),$$

$$\mathcal{J} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix},$$

$$W = -\lambda_e \begin{bmatrix} 0 \\ 1 \end{bmatrix},$$

$$g = \frac{\lambda_e}{T_2} \begin{bmatrix} 0 \\ 1 \end{bmatrix},$$

Making use of the lift of IPHS, let $p = [p_1, p_2]^{tr}$, we obtain the expression of the closed-loop contact Hamiltonian $\hat{\mathrm{K}} = \mathrm{K}_0 + \Phi \circ \mathrm{K}_c$ given by

$$\begin{aligned} \mathrm{K}_0(x,p) &= -\mathcal{R}(x, \tfrac{\partial U}{\partial x})p^{tr}\mathcal{J}T(x) + (\tfrac{\partial U}{\partial x} - p)^{tr}W \\ &= -\lambda(\tfrac{1}{T_2} - \tfrac{1}{T_1})(T_1p_2 - T_2p_1) - \lambda_e(T_2 - p_2) \end{aligned} \tag{5.21}$$

$$\mathrm{K}_c(x,p) = (\frac{\partial U}{\partial x} - p)^{tr}g = \frac{\lambda_e}{T_2}(T_2 - p_2) \tag{5.22}$$

Then the closed-loop contact vector field is $\hat{X}_{\mathrm{K}} = X_{\mathrm{K}_0} + (\Phi^{'} \circ \mathrm{K}_c) X_{\mathrm{K}_c}$, where in canonical coordinates (x_0, x, p), the vector field X_{K_0}, X_{K_c} are expressed as

$$X_{\mathrm{K}_0} = \begin{bmatrix} \mathrm{K}_0 - p^{tr}\frac{\partial \mathrm{K}_0}{\partial p} \\ -\frac{\partial \mathrm{K}_0}{\partial p} \\ p^{tr}\frac{\partial \mathrm{K}_0}{\partial x_0} + \frac{\partial \mathrm{K}_0}{\partial x} \end{bmatrix} = \begin{bmatrix} -T_2\lambda_e \\ -\lambda T_2(\frac{1}{T_2} - \frac{1}{T_1}) \\ \lambda T_1(\frac{1}{T_2} - \frac{1}{T_1}) - \lambda_e \\ \lambda(\frac{T_2 p_1}{T_1^2} - \frac{p_2}{T_2})\frac{\partial T_1}{\partial S_1} \\ \lambda(\frac{T_1 p_2}{T_2^2} - \frac{p_1}{T_1})\frac{\partial T_2}{\partial S_2} - \lambda_e \frac{\partial T_2}{\partial S_2} \end{bmatrix}$$

$$X_{\mathrm{K}_c} = \begin{bmatrix} \mathrm{K}_c - p^{tr}\frac{\partial \mathrm{K}_c}{\partial p} \\ -\frac{\partial \mathrm{K}_c}{\partial p} \\ p^{tr}\frac{\partial \mathrm{K}_c}{\partial x_0} + \frac{\partial \mathrm{K}_c}{\partial x} \end{bmatrix} = \begin{bmatrix} \lambda_e \\ 0 \\ \frac{\lambda_e}{T_2} \\ 0 \\ \frac{p_2 \lambda_e}{T_2^2}\frac{\partial T_2}{\partial S_2} \end{bmatrix}$$

Recalling the equilibrium conditions of closed-loop contact vector field (5.6), (5.7) and (5.8) at the equilibrium point (x_0^*, x^*, p^*), we have

$$\hat{\mathrm{K}} \mid_{(x_0^*, x^*, p^*)} = (\mathrm{K}_0 + \Phi(\mathrm{K}_c) \mid_{(x_0^*, x^*, p^*)} = 0$$

$$\frac{\partial \hat{\mathrm{K}}}{\partial p} \mid_{(x_0^*, x^*, p^*)} = \left(\begin{bmatrix} \frac{\partial \mathrm{K}_0}{\partial p_1} \\ \frac{\partial \mathrm{K}_0}{\partial p_2} \end{bmatrix} + \Phi'(\mathrm{K}_c) \begin{bmatrix} \frac{\partial \mathrm{K}_c}{\partial p_1} \\ \frac{\partial \mathrm{K}_c}{\partial p_2} \end{bmatrix} \right) \mid_{(x_0^*, x^*, p^*)} = 0$$

$$\left(\frac{\partial \hat{\mathrm{K}}}{\partial x} + (p^*)^{tr}\frac{\partial \hat{\mathrm{K}}}{\partial x_0} \right) \mid_{(x_0^*, x^*, p^*)} = \left(\begin{bmatrix} \frac{\partial \mathrm{K}_0}{\partial x_1} \\ \frac{\partial \mathrm{K}_0}{\partial x_2} \end{bmatrix} + \Phi'(\mathrm{K}_c) \begin{bmatrix} \frac{\partial \mathrm{K}_c}{\partial x_1} \\ \frac{\partial \mathrm{K}_c}{\partial x_2} \end{bmatrix} \right) \mid_{(x_0^*, x^*, p^*)} = 0$$

or equivalently

$$-\lambda(\frac{1}{T_2} - \frac{1}{T_1})(T_1 p_2^* - T_2 p_1^*) - \lambda_e(T_2 - p_2^*) + \Phi\left(\frac{\lambda_e}{T_2}(T_2 - p_2^*)\right) = 0$$

$$\begin{bmatrix} \lambda T_2(\frac{1}{T_2} - \frac{1}{T_1}) \\ -\lambda T_1(\frac{1}{T_2} - \frac{1}{T_1}) + \lambda_e \end{bmatrix} + \Phi'\left(\frac{\lambda_e}{T_2}(T_2 - p_2^*)\right) \begin{bmatrix} 0 \\ -\frac{\lambda_e}{T_2} \end{bmatrix} = 0$$

and thus at the equilibrium point, we have

$$T_1^* = T_2^* = p_1^* = p_2^* \tag{5.23}$$

$$\mathrm{K}_c(x^*, p^*) = 0 \tag{5.24}$$

$$\Phi(\mathrm{K}_c(x^*, p^*)) = \Phi(0) = 0 \tag{5.25}$$

$$\Phi'(\mathrm{K}_c(x^*, p^*)) = \Phi'(0) = T^* \tag{5.26}$$

Then, by making use of the expression (5.12) and the equations above (5.23), (5.24), (5.25), and (5.26), we obtain the expression of the Jacobian matrix of closed-loop contact vector field $\mathrm{D}\hat{X}_{\mathrm{K}}$ in canonical coordinates (x_0, x, p). Namely, at equilibrium point, the expression of $\mathrm{D}\hat{X}_{\mathrm{K}}(x_0^*, x^*, p^*)$ defined as in (5.27).

$$\mathrm{D}\hat{X}_{\mathrm{K}}(x^*, x^*, p^*) =$$
$$\begin{bmatrix} 0 & 0 & -\lambda_e \frac{\partial T_2}{\partial S_2} + \frac{\lambda_e^2}{T^*} \frac{\partial T_2}{\partial S_2} \Phi'' & 0 & -\frac{\lambda_e^2}{T^*} \Phi'' \\ 0 & -\frac{\lambda}{T^*} \frac{\partial T_1}{\partial S_1} & \frac{\lambda}{T^*} \frac{\partial T_2}{\partial S_2} & 0 & 0 \\ 0 & \frac{\lambda}{T^*} \frac{\partial T_1}{\partial S_1} & -\left(\frac{\lambda+\lambda_e}{T^*}\right) \frac{\partial T_2}{\partial S_2} + \frac{\lambda_e^2}{T_2^2} \frac{\partial T_2}{\partial S_2} \Phi'' & 0 & -\frac{\lambda_e^2}{T^{*2}} \Phi'' \\ 0 & -\frac{2\lambda}{T^*} \left(\frac{\partial T_1}{\partial S_1}\right)^2 & \frac{2\lambda}{T^*} \frac{\partial T_1}{\partial S_1} \frac{\partial T_2}{\partial S_2} & \frac{\lambda}{T^*} \frac{\partial T_1}{\partial S_1} & -\frac{\lambda}{T^*} \frac{\partial T_1}{\partial S_1} \\ 0 & \frac{2\lambda}{T^*} \frac{\partial T_1}{\partial S_1} \frac{\partial T_2}{\partial S_2} & \left[-\frac{2(\lambda+\lambda_e)}{T^*} + \frac{\lambda_e^2}{T^{*2}} \Phi''\right] \left(\frac{\partial T_2}{\partial S_2}\right)^2 + \lambda_e \frac{\partial^2 T_2}{\partial S_2^2} & -\frac{\lambda}{T^*} \frac{\partial T_2}{\partial S_2} & \left[\frac{\lambda+\lambda_e}{T^*} - \frac{\lambda_e^2}{T^{*2}} \Phi''\right] \frac{\partial T_2}{\partial S_2} \end{bmatrix} \tag{5.27}$$

with $\Phi'' = \Phi''(\mathrm{K}_c(x^*, p^*)) = \Phi''(0)$ and $T^* = T_1^* = T_2^*$. The determinant of the Jacobian matrix $\mathrm{D}\hat{X}_{\mathrm{K}}(x_0^*, x^*, p^*)$ is computed as

$$\det(\delta \mathrm{I}_n - \mathrm{D}\hat{X}_{\mathrm{K}}) = \delta \begin{bmatrix} -\delta^4 + \left(\frac{\lambda_e^2}{T^{\star 2}} \Phi'' B + A^2 + C^2 + 2D\right) \delta^2 + \\ \left(\frac{2\lambda^3 \lambda_e^2}{T^5} \left(\frac{\partial T_2}{\partial S_2}\right)^2 \left(\frac{\partial T_1}{\partial S_1}\right)^2 \Phi'' - \frac{\lambda_e^2}{T^{\star 2}} \Phi'' B A^2 + A^2 C^2 - 2ACD + D^2\right) \end{bmatrix}$$

(5.28)

where

$$A = \frac{\lambda}{T^*}\frac{\partial T_1}{\partial S_1} \tag{5.29}$$

$$B = \frac{2\lambda}{T^*}(\frac{\partial T_2}{\partial S_2})^2 - \lambda_e\frac{\partial^2 T_2}{\partial S_2^2} + \frac{2\lambda_e}{T^*}(\frac{\partial T_2}{\partial S_2})^2 - \frac{\lambda_e^2}{T^{*2}}(\frac{\partial T_2}{\partial S_2})^2\Phi'' \tag{5.30}$$

$$C = (\frac{\lambda}{T^*} + \frac{\lambda_e}{T^*})\frac{\partial T_2}{\partial S_2} - \frac{\lambda_e^2}{T_2^2}\frac{\partial T_2}{\partial S_2}\Phi'' \tag{5.31}$$

$$D = \frac{\lambda^2}{T^{*2}}\frac{\partial T_2}{\partial S_2}\frac{\partial T_1}{\partial S_1} \tag{5.32}$$

As mentioned in Sect. 5.3.2, the point zero is one of the eigenvalues of the Jacobian matrix $\mathrm{D}\hat{X}_\mathrm{K}(x_0^*, x^*, p^*)$ and the other $2n$ eigenvalues are symmetrical with respect to the imaginary axis. Therefore the eigenvalues of the Jacobian matrix $\mathrm{D}\hat{X}_\mathrm{K}(x_0^*, x^*, p^*)$ are denoted as

$$\begin{aligned}
\delta_1 &= re^{j\theta}\\
\delta_2 &= re^{-j\theta}\\
\delta_3 &= -re^{j\theta}\\
\delta_4 &= -re^{-j\theta}\\
\delta_5 &= 0
\end{aligned}$$

Hence the determinant of the Jacobian matrix $\mathrm{D}\hat{X}_\mathrm{K}(x_0^*, x^*, p^*)$ should be able to write in the following way:

$$\begin{aligned}
\det(\delta \mathrm{I}_n - D\hat{X}_\mathrm{K}) &= \delta(\delta-\delta_1)(\delta-\delta_2)(\delta-\delta_3)(\delta-\delta_4)\\
&= \delta\left[\delta^4 - 2r(1-2sin^2\theta)\delta^2 + r^4\right]
\end{aligned} \tag{5.33}$$

Comparing the two polynomials above (5.28) and (5.33), we derive the symmetrical poles:

$$r = (\lambda\lambda_e\frac{\partial T_1}{\partial S_1}\frac{\partial T_2}{\partial S_2})^{\frac{1}{2}}\frac{1}{T}(\frac{-2\lambda_e^2\Phi_0''^2}{T^2} + \frac{4\lambda_e\Phi_0''}{T} - 1)^{\frac{1}{4}}$$

$$\theta = \frac{1}{2}arccos\left(\frac{\lambda^2(\frac{\partial T_1}{\partial S_1})^2 + (\lambda+\lambda_e)^2(\frac{\partial T_2}{\partial S_2})^2 + 2\lambda^2\frac{\partial T_1}{\partial S_1}\frac{\partial T_2}{\partial S_2}}{2\lambda\lambda_e\frac{\partial T_1}{\partial S_1}\frac{\partial T_2}{\partial S_2}}\right)$$

It is noticeable that we find a relationship between the non-zero poles and the value of the feedback Φ at equilibrium. Evidently, it is not the feedback Φ itself but its second derivative $\Phi^{''}$ which appears in the expression of the non-zero poles. Besides, among the four expressions above (5.29), (5.30), (5.31), and (5.32), the expression A and D are independent of the feedback $\Phi^{''}(0)$, thus they do not affect the influence of the feedback on the non-zero poles. On the contrary, owing to the existence of $\Phi^{''}(0)$ in the expressions of B and C, the non-zero poles depend also on $(\Phi^{''}(0))^2$ but not on $\Phi^{''}(0)$. In addition, we find that once the feedback Φ has been chosen, the expression of r and θ can be determined and consequently the $2n$ non-zero poles (n stable and n unstable) will be placed properly in the complex plane.

Afterwards we continue to analyze the stability of the heat exchanger, using the center manifold theory shown in Sect. 5.3.3. Obviously, there should be $2n+1$ eigenvalues of the Jacobian matrix $\mathrm{D}\hat{X}_{\mathrm{K}}$ which implies that there should be $2n+1$ poles in the complex plane. Among all the poles, there is a zero pole and the other $2n$ poles are symmetrical about the imaginary axis. Therefore, only the poles in the left-half plane are stable. Therefore, while analyzing the stability of the closed-loop contact system, we only consider n stable poles located in the left-half complex plane. The invariant Legendre submanifolds of interest, denoted as L_{U_d}, are given in canonical coordinates (x_0, x, p) as

$$L_{U_d} : \begin{cases} x_0^d &= U_d(x) \\ x &= x \\ p^d &= \frac{\partial U_d}{\partial x}(x) \end{cases}$$

Furthermore, the closed-loop contact Hamiltonian $\hat{\mathrm{K}}$ is zero on the Legendre submanifold

$$\hat{\mathrm{K}}\Big|_{L_{U_d}} = (\mathrm{K}_0 + \Phi \circ \mathrm{K}_c)|_{L_{U_d}} = 0$$

This equation becomes a quadratic partial differential equation of first order, with two variables:

$$\mathrm{K}_0(x, \frac{\partial U_d}{\partial x}(x)) + \Phi \circ \mathrm{K}_c(x, \frac{\partial U_d}{\partial x}(x)) = -c_F \tag{5.34}$$

where c_F is a constant. Assume that $\Phi(\chi) = \mathcal{K}\chi$ with $\mathcal{K}$ constant and the equation (5.34) becomes

$$[\lambda_e - \lambda T_1(\frac{1}{T_2} - \frac{1}{T_1}) - \frac{\mathcal{K}\lambda_e}{T_2}](\frac{\partial U_d}{\partial x_2}) + \lambda T_2(\frac{1}{T_2} - \frac{1}{T_1})(\frac{\partial U_d}{\partial x_1}) = \lambda_e T_2 - k\lambda_e$$

This quadratic partial differential equation of first order and with two variables, can be solved by the method of characteristics (Myint-U and Debnath 2007), with the initial condition (5.23), (5.24), (5.25), and (5.26). Thus, the solution of $U_d(x_1, x_2)$ can be written as

$$\begin{aligned} U_d(x_1,x_2) = \quad & \tfrac{-\mathcal{K}\lambda_e x_1}{\lambda} - \tfrac{\mathcal{K}\lambda_e}{\lambda}\tfrac{T_2}{T_1'}\ln(T_1-T_2) + \tfrac{\mathcal{K}\lambda_e}{\lambda}\tfrac{T_2^o}{T_1^{o\prime}}\ln(T_1^o-T_2^o) \\ & + \tfrac{\lambda_e T_2^3}{2T_2'[(\lambda+\lambda_e)T_2-\lambda T_1-\mathcal{K}\lambda_e]} - \tfrac{\lambda_e T_2^{o3}}{2T_2^{o\prime}[(\lambda+\lambda_e)T_2^o-\lambda T_1^o-\mathcal{K}\lambda_e]} \\ & + f\begin{pmatrix} x_2 - \tfrac{(\lambda+\lambda_e)}{\lambda}x_1 \\ -\tfrac{(\lambda+\lambda_e)}{\lambda}\tfrac{T_2}{T_1'}\ln(T_1-T_2) + \tfrac{(\lambda+\lambda_e)}{\lambda}\tfrac{T_2^o}{T_1^{o\prime}}\ln(T_1^o-T_2^o) \\ +\tfrac{\lambda_e T_1+\mathcal{K}\lambda_e}{(\lambda+\lambda_e)T_2'}\ln[(\lambda+\lambda_e)T_2-(\lambda_e T_1+\mathcal{K}\lambda_e)] \\ -\tfrac{\lambda_e T_{o1}+\mathcal{K}\lambda_e}{(\lambda+\lambda_e)T_2^{o\prime}}\ln[(\lambda+\lambda_e)T_2^o-(\lambda_e T_1^o+\mathcal{K}\lambda_e)] \end{pmatrix} \end{aligned} \tag{5.35}$$

with T_2^o and T_1^o are the reference temperature of subsystem 1 and 2. So there exists one stable and one unstable submanifold of dimension n, which are Legendre submanifolds. Based on the center manifold theory, we can construct the characteristic subspace associated with the stable poles, denoted as Π^-, as

$$\Pi^- = \ker(\delta_3 \mathrm{I}_5 - \mathrm{D}\hat{X}_\mathrm{K}) \oplus \ker(\delta_4 \mathrm{I}_5 - \mathrm{D}\hat{X}_\mathrm{K})$$

Assume that the kernel of the matrix $\delta_3 \mathrm{I}_5 - \mathrm{D}\hat{X}_\mathrm{K}$ is a vector of dimension $\mathbb{R}^{5\times 1}$, denoted as $v = [v_0, v_1, v_2, v_3, v_4]^{tr}$ which fulfills

$$(\delta_3 \mathrm{I}_s - D\hat{X}_\mathrm{K})v = [0,0,0,0,0]^{tr}$$

In the same way, we consider the kernel of the matrix $\delta_4 \mathrm{I}_5 - \mathrm{D}\hat{X}_\mathrm{K}$ as a vector of dimension $\mathbb{R}^{5\times 1}$, noted as $v^{'} = [v_0^{'}, v_1^{'}, v_2^{'}, v_3^{'}, v_4^{'}]^{tr}$ and we obtain the expression of the characteristic subspace associated with stable poles Π^-:

$$\Pi^- = \left\{ u \in \mathbb{R}^{5\times 1} \mid u = k_1 v + k_2 v^{'}, \forall k_1, k_2 \in \mathbb{R} \right\}$$

Since the invariant Legendre submanifold is tangent with the subspace Π^- at the equilibrium point, i.e.,

$$T_{x*} L_{Ud} = \Pi^-$$

We have

$$\begin{bmatrix} dU_d(x^*) \\ dx(x^*) \\ d^2U_d(x^*) \end{bmatrix} = w_1 dx_1 + w_2 dx_2$$

Obviously, the rank of the matrix $Y = [v, v^{'}, w_1, w_2]^{tr}$ is 2. By computing the determinant of the matrix of partial derivatives of Y, we finally obtain the expression of $\frac{\partial U_d}{\partial x_1}(x^*)$ and $\frac{\partial U_d}{\partial x_2}(x^*)$:

$$\frac{\partial U_d}{\partial x_1}(x^*) = -\frac{\mathcal{K}\lambda_e}{\lambda} - \frac{(\lambda+\lambda_e)}{\lambda} f^{'}(x_2^* - \frac{(\lambda+\lambda_e)}{\lambda} x_1^*) \tag{5.36}$$

$$\frac{\partial U_d}{\partial x_2}(x^*) = f^{'}(x_2^* - \frac{(\lambda+\lambda_e)}{\lambda} x_1^*) \tag{5.37}$$

At the equilibrium point, we have $\frac{\partial U_d}{\partial x_1}(x^*) = T^*$ and $\frac{\partial U_d}{\partial x_2}(x^*) = T^*$. Therefore we infer that

$$\mathcal{K} = T^* \tag{5.38}$$

It should be remarked that U_d depends linearly on the structure-preserving feedback $\Phi_0^{''}$. Once the feedback Φ has been chosen, the expression $dU_d(x^\star)$ can be determined. These two equations above provide us a general idea while choosing the desired invariant Legendre submanifolds L_{U_d} and the structure-preserving feedback.

Then we compute the availability function (5.19) as

$$A(x) = U_d(x) - U_d(x^\star) - k^{tr}(x - x^\star) \tag{5.39}$$

Moreover, this equation satisfies the conditions (5.16) and (5.17), and the time derivative of A can be derived as

$$\begin{aligned} \frac{dA}{dt} &= (\frac{\partial U_d}{\partial x}(x) - \frac{\partial U_d}{\partial x}(x^*))^{tr} \frac{dx}{dt} \\ &= -\gamma \frac{\partial U}{\partial x}(x^*) J \frac{\partial U}{\partial x}(x) \{S, U\}_J + \left(\frac{\partial U}{\partial x}(x) - \frac{\partial U}{\partial x}(x^*)\right)^{tr} g(x,u) \\ &= -\frac{\lambda T^*}{T_1 - T_2}(T_1 - T_2)^2 + (T_2 - T^*)\frac{u - T_2}{uT_2} \\ &= -\frac{\lambda T^*}{T_1 - T_2}(T_1 - T_2)^2 + (T_2 - T^*)\frac{\mathcal{K} - T_2}{\mathcal{K}T_2} \end{aligned} \tag{5.40}$$

The expression in equation (5.40) equals zero at the equilibrium point, while outside the equilibrium point, the first term is always less than zero. Hence the closed-loop system will converge asymptotically to the equilibrium point if the second term is also less than zero, that is

$$(T_2 - T^*)\frac{\mathcal{K} - T_2}{\mathcal{K}T_2} \leqslant 0$$

The easiest way is to let $\mathcal{K} = T^*$ which matches with the previous result (5.38). Therefore, we have $\Phi(\chi) = T^*\chi$ and the structure-preserving feedback $\alpha(\chi) = T^*$.

5.5 Example II: a simple isothermal chemical reaction network

Consider a simple isothermal reaction network given as

$$X_1 \underset{k_1^b}{\overset{k_1^f}{\rightleftharpoons}} X_2$$

Defining the state vector $x = [x_1, x_2]^{tr}$ with x_1, x_2 the concentration of species X_1 and X_2, the Hamiltonian function $\mathrm{H} = U$ with U the internal energy of system, and the co-state vector $\frac{\partial U}{\partial x} = \mu$ with $\mu = [\mu_1, \mu_2]^{tr}$ the vector of chemical potentials. The input/output concentration flow can be defined as $gu = [0, g_2]^{tr}u$ with g_2 constant and $u(t)$ a time-dependent function. Since the network is isothermal, the dynamics can be written as

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \end{bmatrix} = -\begin{bmatrix} \kappa_1 & -\kappa_1 \\ -\kappa_1 & \kappa_1 \end{bmatrix} \mathrm{Exp}\begin{pmatrix} \mu_1 \\ \mu_2 \end{pmatrix} + \begin{bmatrix} 0 \\ g \end{bmatrix} u \tag{5.41}$$

with $\mu_i = \ln \frac{x_i}{x_i^*}$, $i = 1, 2$ and $\kappa_1 = k_1^f x_1^* = k_1^b x_2^*$, where x_1^* and x_2^* are the value of the thermodynamic equilibrium.

Let $p = [p_1, p_2]^{tr}$, then the shaped contact Hamiltonian $\hat{\mathrm{K}} = \mathrm{K}_0 + \Phi \circ \mathrm{K}_c$ is given by

$$\begin{aligned} \mathrm{K}_0 &= p^{tr}\begin{bmatrix} \kappa_1 & -\kappa_1 \\ -\kappa_1 & \kappa_1 \end{bmatrix} \mathrm{Exp}\begin{pmatrix} \mu_1 \\ \mu_2 \end{pmatrix} \\ &= (p_1 - p_2)\kappa_1(\exp \mu_1 - \exp \mu_2) \end{aligned} \tag{5.42}$$

$$\begin{array}{ll} \mathrm{K}_c & = (\frac{\partial U}{\partial x} - p)^{tr} g u \\ & = (\mu_2 - p_2) g_2 u \end{array} \tag{5.43}$$

By using the equilibrium conditions (5.6, (5.7), (5.8), at equilibrium,

$$\mu_1^* = \mu_2^* = p_1^* = p_2^* \tag{5.44}$$

$$\mathrm{K}_c(x^*, p^*) = 0 \tag{5.45}$$

$$\Phi(\mathrm{K}_c(x^*, p^*)) = \Phi(0) = 0 \tag{5.46}$$

$$\Phi'(\mathrm{K}_c(x^*, p^*)) = \Phi'(0) = 0 \tag{5.47}$$

The invariant Legendre submanifolds of interest, denoted as L_{U_d}, are in canonical coordinates (x_0, x, p) given as

$$L_{U_d} : \left\{ \begin{array}{ccc} x_0^d & = & U_d(x) \\ x & = & x \\ p^d & = & \frac{\partial U_d}{\partial x}(x) \end{array} \right.$$

Since the closed-loop contact Hamiltonian $\hat{\mathrm{K}}$ is zero on the Legendre submanifold, we have $\hat{\mathrm{K}}|_{L_{U_d}} = (\mathrm{K}_0 + \Phi \circ \mathrm{K}_c)|_{L_{U_d}} = 0$. Assuming that $\Phi(\chi) = \rho\chi^2$, then we obtain a partial differential equation with two variables,

$$\mathrm{K}_0(x, \frac{\partial U_d}{\partial x}(x)) + \Phi \circ \mathrm{K}_c(x, \frac{\partial U_d}{\partial x}(x)) = 0$$

which can be developed as

$$\begin{array}{l} [\kappa_1(\exp \mu_1 - \exp \mu_2)] \frac{\partial U}{\partial x_1} + [-\kappa_1(\exp \mu_1 - \exp \mu_2) - 2\rho\mu_2 g_2^2 u^2] \frac{\partial U}{\partial x_2} + \rho g_2^2 u^2 (\frac{\partial U}{\partial x_2})^2 \\ = -\rho\mu_2^2 g_2^2 u^2 \end{array}$$

By using the method of characteristics (Myint-U and Debnath 2007), with the equilibrium condition $\mu_1^* = \mu_2^*$, the solution of $U_d(x_1, x_2)$ can be written as

$$U_d(x_1,x_2) = x_1(\mu_1 - q) + \frac{x_1}{\kappa_1(\exp\mu_1 - \exp\mu_2)}(-2\rho\mu_2 g_2^2 u^2 + 2\rho g_2^2 u^2 q) - \rho\mu_2^2 g_2^2 u^2 \quad (5.48)$$

with $q = \frac{(x_1+x_2)\kappa_1(\exp\mu_1 - \exp\mu_2) + 2\rho\mu_2 g_2^2 u^2 x_1}{2\rho g_2^2 u^2 x_1}$. At equilibrium point, we have $\frac{\partial U_d}{\partial x_1} = \frac{\partial U_d}{\partial x_2} = \mu^*$, thus we could infer that

$$\rho = \frac{\kappa_1}{2g_2^2 u^2}$$

If we compute the availability function, we will get the same result. Therefore, we have $\Phi(\chi) = \frac{\kappa_1}{2g_2^2 u^2}\chi^2$ and the structure-preserving feedback $\alpha(\chi) = \frac{\kappa_1}{g_2^2 u^2}\chi$.

5.6 Conclusion

In this chapter, we considered several control approaches based on structure-preserving state feedback. After recalling the previous work (Kotyczka 2013), the local stability of the closed-loop contact system has been studied. Furthermore, the invariant stable submanifold Legendre has been formulated. Finally, the possibility of constructing an availability function as candidate Lyapunov function on the Legendre submanifold has been discussed. With these control approaches, we are able to find some conditions while formulating the structure-preserving feedback. These results have been illustrated on two examples: the heat exchanger and the simple chemical reaction network.

Chapter 6

Conclusion

In this chapter, we will review the main contributions and findings presented in Chapters 2-5. We also provide suggestions for future research in this chapter.

6.1 General conclusion

Some different approaches to the modeling and analysis of non-isothermal chemical reaction networks have been studied in this dissertation.

The first approach studied is the irreversible port-Hamiltonian formulation generated by the total internal energy in Chapter 2, which was introduced in (Ramirez, Maschke and Sbarbaro 2013b). The modeling and thermodynamic analysis for non-isothermal mass action kinetics chemical reaction networks have been studied, including the conditions for existence of a thermodynamic equilibrium and their asymptotic stability.

The second approach studied is the quasi port-Hamiltonian system generated by the total entropy in Chapter 3. We found that this new quasi port-Hamiltonian system is very suitable for the modeling of non-isothermal chemical reaction networks. The thermodynamic analysis is carried out as well, including the characterization of equilibria and their asymptotic stability. Moreover, the modeling of interconnection of chemical reaction networks has been explored in Chapter 4. Two different modeling approaches have been developed in quasi port-Hamiltonian form. It has been proved that the two modeling approaches are equivalent by eliminating the mass kinetics and power port constraints.

The third approach studied is the control contact system with structure-preserving feedback in Chapter 5, which was introduced in (Ramirez 2012). It is shown in this dissertation that the control contact system with a specific structure-preserving feedback can be used for the modeling and thermodynamic analysis of non-isothermal chemical reaction networks. A series of control designs by structure-preserving state feedback have been studied in order to add some constraints. Local stability has been carried out to determine the structure-preserving state feedback,

through the equilibrium conditions for the closed-loop contact system and the Jacobian matrix of the closed-loop contact vector field. Furthermore, the conditions for local and partial stability on the closed-loop invariant Legendre submanifold have been given, in order to determine the controlled contact Hamiltonian and to verify the correctness of the structure-preserving feedback.

6.2 Future research

Some possible research directions are the following.

- For the modeling of open chemical reaction networks: future research includes different formulations of the external ports, such as the concentration flows or the heat (energy) flow.
- For the interconnection of chemical reaction networks: it is of interest to further study the thermodynamic analysis of the interconnected chemical reaction networks. For example, one of the interesting subjects is the analysis of the equilibrium (or thermodynamic equilibrium), and another is the entropy flow (or the energy flow) in the interconnected chemical reaction network.
- For the contact system: in this dissertation, we have applied the control contact system with structure-preserving feedback on a simple chemical reaction network. The research questions about the application to more complicated chemical reaction networks, are still open. With more chemical species in the chemical reaction network, the partial differential equation (5.15) is certainly more difficult to solve.

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Summary

In this dissertation, we use different approaches to the geometric modeling and analysis of non-isothermal mass action kinetics chemical reaction networks. Generally speaking, these approaches can be divided into two classes: one based on the port-Hamiltonian system theory, and the other based on the theory of contact systems.

The first approach studied is the irreversible port-Hamiltonian formulation generated by the total internal energy, which was introduced in (Ramirez, Maschke and Sbarbaro 2013b). Beginning with the overview of mathematical structure of chemical reaction networks in the non-isothermal case, we establish the irreversible port-Hamiltonian formulation of non-isothermal chemical reaction networks and then investigate its thermodynamic analysis, including the conditions for existence of a thermodynamic equilibrium and their asymptotic stability.

The second approach studied is the quasi port-Hamiltonian system generated by the total entropy. In this port-Hamiltonian system, not only the energy balance equations but also the entropy balance equations will be used. Therefore, we found that this new quasi port-Hamiltonian system is very suitable for the modeling of non-isothermal chemical reaction networks. The thermodynamic analysis is carried out as well, including the characterization of equilibria and their asymptotic stability.

Otherwise, based on the new quasi port-Hamiltonian system, the modeling of interconnection of chemical reaction networks has been explored. This is of importance in the compositional modeling of complex chemical reaction networks as often encountered in systems biology and chemical engineering. In order to develop a port-Hamiltonian structure for interconnected chemical reaction networks, we offer two ways to deal with interconnection by shared species; one called the network interconnection arising from shared boundary species and the other called the interconnection arising from *power-port interconnection*. Subsequently, it is proved that

the two modeling approaches are equivalent by eliminating the power port constraints and the Lagrangian multipliers in the dynamics.

The third approach studied is the control contact system with structure-preserving feedback, which was introduced in (Ramirez 2012). It is shown in this dissertation that the control contact system with a specific structure-preserving feedback can be used for the modeling and thermodynamic analysis of non-isothermal chemical reaction networks. A series of control designs by structure-preserving state feedback has been studied in order to add some constraints. Local stability analysis has been carried out to determine the structure-preserving state feedback, through the equilibrium conditions for the closed-loop contact system and the Jacobian matrix of the closed-loop contact vector field. Furthermore, conditions for local and partial stability on the closed-loop invariant Legendre submanifold have been given, in order to determine the controlled contact Hamiltonian and to verify the correctness of the structure-preserving feedback.

Samenvatting

In dit proefschrift worden verschillende benaderingen gebruikt voor de meetkundige modellering en analyse van chemische reactienetwerken met variërende temperatuur. Ruw gesproken kunnen deze benaderingen in twee klassen worden verdeeld: de ene gebaseerd op poort-Hamiltonse systeemtheorie, en de ander gebaseerd op de theorie van contactsystemen.

De eerste aanpak is de irreversibele poort-Hamiltonse formulering op basis van de interne energie, die geintroduceerd werd in Ramirez, Maschke en Sbarbaro in 2013. Beginnend met een overzicht van de wiskundige structuur van chemische reactienetwerken in het niet-isothermische geval wordt een irreversibele poort-Hamiltonse formulering van niet-isothermische reactienetwerken gegeven. Daarna volgt een thermodynamische analyse, inclusief de voorwaarden voor het bestaan van een thermodynamisch evenwicht en de asymptotische stabiliteit van de verzameling van thermodynamische evenwichtspunten. De tweede benadering betreft de quasi poort-Hamiltonse modellering met behulp van de totale entropie. In dit poort-Hamiltonse systeem wordt niet alleen de energiebalans maar ook de entropiebalansvergelijking gebruikt. Deze nieuwe quasi poort-Hamiltonse formulering is bijzonder geschikt voor de modellering van niet-isothermische chemische reactienetwerken. Ook de thermodynamische analyse wordt in dit kader uitgevoerd, in het bijzonder de karakterisatie van evenwichtspunten en hun asymptotische stabiliteit.

Gebaseerd op deze nieuwe quasi poort-Hamiltonse formulering wordt verder de interconnectie van chemische reactienetwerken bestudeerd. Dit is van groot belang voor een compositionele modellering van complexe chemische reactienetwerken zoals vaak voorkomend in systeembiologie en chemische technologie. Voor de poort-Hamiltonse formulering van de interconnectie van chemische reactienetwerken worden twee benaderingen gegeven. De ene is gebaseerd op de

netwerkinterconnectie via gedeelde chemische stoffen, en de tweede is gebaseerd op vermogensinterconnectie via fluxen en chemische potentialen. Door middel van het elimineren van de vermogenspoortbeperkingen en hun Lagrange multiplicatoren wordt aangetoond dat de twee aanpakken equivalent zijn.

Tenslotte wordt de regeling van contactsystemen door middel van structuurbehoudende terugkoppeling bestudeerd, zoals geintroduceerd in Ramirez in 2012. Er wordt aangetoond dat contactsystemen met specifieke structuurbehoudende terugkoppeling kunnen worden gebruikt voor de thermodynamische modellering en analyse van niet-isothermische reactienetwerken. Een aantal regelontwerpen die hierop gebaseerd zijn worden bestudeerd. Een lokale stabiliteitsanalyse wordt uitgevoerd om de structuurbehoudende terugkoppeling te bepalen, op basis van evenwichtsvoorwaarden en de Jacobimatrix van het teruggekoppelde systeem. Verder worden voorwaarden voor lokale en gedeeltelijke stabiliteit ten opzichte van de gesloten-lus invariant Legendre deelvarieteit gegeven, alsmede de gesloten-lus contact Hamiltonfunctie.

Résumé

Dans cette thèse, on utilise différentes méthodes pour modéliser géométriquement et analyser des réseaux de réactions chimiques de cinétique d'action non-isothermes. En générale, ces méthodes peuvent être divisées en deux groupes: l'une basée sur la théorie du système port-Hamiltonien et l'autre basée sur la théorie du système de contact.

La première méthode discutée dans cette thèse est le système port-Hamiltonien irréversible généré par l'énergie interne totale, appelé IPHS et introduit dans (Ramirez, Maschke and Sbarbaro 2013b). On commence par les études sur la structure mathématique des réseaux de réactions chimiques dans le cas non-isotherme, et puis on établit le système port-Hamiltonien irréversible des réseaux de réactions chimiques non isothermes. On étudie ensuite sur ses propriétés thermodynamiques, y compris les conditions d'existence du point d'équilibre thermodynamique et la stabilité asymptotique du système.

La deuxième méthode étudiée est le système quasi port-Hamiltonien généré par l'entropie totale du système. Dans ce système quasi port-Hamiltonien, on utilise non seulement les équations du bilan d'énergie mais aussi les équations du bilan d'entropie. En conséquence, on trouve que ce nouveau système est très approprié pour la modélisation de réseaux de réactions chimiques non-isothermes. Les analyses thermodynamiques sont également effectuées, y compris la discussion sur les sous-ensembles des points d'équilibre thermodynamique et la stabilité asymptotique du système.

En plus, la modélisation de l'interconnection des réseaux de réactions chimiques a été explorée. Afin de développer une structure port-Hamiltonienne pour un réseau interconnecté par deux réseaux de réactions chimiques, nous proposons deux façons possible: l'une s'appelle l'interconnection par les espèces chimiques communes aux frontières et l'autre s'appelle l'interconnection du port de puissance. En

fait, on prouve que les deux façons sont équivalentes en éliminant les contraintes du port de puissance et les multiplicateurs Lagrangiens dans les équations dynamiques du système.

La troisième méthode étudiée est le système de contact avec un retour d'état préservant la structure, qui a été introduit dans (Ramirez 2012). Une synthèse de contrôle sur le système de contact contrôlé a été discutée afin d'ajouter certaines contraintes sur le retour d'état préservant la structure spécifique. On étudie la stabilité locale, y compris les conditions d'équilibre du système de contact en boucle fermée, la matrice Jacobienne du champ de vecteur de contact en boucle fermée et la sous-variété Legendre invariante en boucle fermée. On étudie aussi la stabilité asymptotique du système via l'équation Lyapunov.